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TABLE OF CONTENTS

EDITORIALS:		Disposal of Sewage with Recovery of Elements of Plant Food for Use in Agriculture. By William McMurtrie.....	156
Cooperation among Chemists and Manufacturers	92	Manufacture and Uses of Cyanamid. By E. J. Pranke	159
The Present State of the Art of Industrial Management	93	CURRENT INDUSTRIAL NEWS:	
ORIGINAL PAPERS:		United States Statistics for 1912.....	161
The Hydrogenation of Oils. By Carleton Ellis.....	95	The Chemical Activities of Belgium.....	161
Boron: Its Properties and Preparation. By E. Weintraub.....	106	The Increased Use of Charcoal Iron.....	161
Acetylene Solvents. By Joseph H. James.....	115	Gilled Tubing.....	161
Tests on the Opacity and Hiding Power of Pigments. By G. W. Thompson.....	120	The Toxicity of White Lead.....	161
An Application of the Electric Resistance Furnace to the Determination of Oxygen in Iron and Steel. By R. H. McMillen.....	123	Tantalum as a Substitute for Platinum.....	162
The Volumetric Determination of Manganese in Rock, Slags, Ores and Spiegels. By F. J. Metzger and L. E. Marrs.....	125	Sulfur in Illuminating Gas.....	162
Antiseptic Tests of Wood Preserving Oils. By A. L. Dean and C. R. Downs.....	126	The Use of Gases for Fire Extinction on Board Ship..	162
The Oxygen Absorption Test for Linseed Oil. By Hans Mannhardt.....	129	A New Timber Preserving Process.....	163
A Rapid and Accurate Gravimetric Method for Determining Milk-Fat in Evaporated Milk and Milk Powders. By E. P. Harding and Guy Parkin.....	131	The Billiter Alkali-Chlorine Cells.....	163
The Rate of the Reaction of Nitrous Acid and Urea in Dilute Solutions. By W. D. Bonner and E. S. Bishop.....	134	Water Purification in the Industries.....	163
The Influence of a Preceding Crop on Nitrification in Soil. By T. Lyttleton Lyon and James A. Bizzell..	136	The Slate-Bed Treatment of Sewage.....	163
A Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils. By E. W. Gaither	138	The Manufacture of Swedish Filter Paper.....	164
A Contribution to Our Methods of Determining Nitrogen in Humus. By Charles B. Lipman and H. F. Pressey.....	143	The Minimization of Fire Risks in the Case of Inflammable Liquids.....	164
LABORATORY AND PLANT:		The British Starch Industry.....	165
The Manufacture and Properties of Sublimed White Lead. By John A. Schaeffer.....	144	The Sulfite Waste Liquor Problem.....	166
A New Form of Laboratory Extraction Apparatus. By A. E. Perkins.....	148	"Sacchulose".....	166
A Device for Controlling Small Electric Furnaces. By Charles Burton Thwing.....	149	NOTES AND CORRESPONDENCE:	
Gas Bubble and Washing Tube for Combustion Apparatus. By H. E. Smith.....	150	A Standard Viscosimeter and Standard Methods for Determining Viscosities—Why not?.....	167
A Modified Extraction Apparatus. By G. M. MacNider.....	150	The Use of a Light Filter Cell in Polarizing High Grade Sugars.....	167
A Reflux Condenser. By S. W. Wiley.....	151	The Analysis of Unsweetened Evaporated Milk.....	168
ADDRESSES:		The Determination of "Volatile" in Coal.....	169
Tar Distillation in the United States—General Development and Recent Progress. By R. P. Perry.....	151	New Chief of Bureau of Chemistry.....	170
		Electrolytic Copper Refining in Norway.....	171
		Growing Use of Ammonium Sulfate in China.....	171
		American Chemical Society Spring Meeting.....	171
		"The Progressive Age" becomes "The Gas Age".....	171
		Obituary—Alfred Bellamy Aubert.....	171
		BOOK REVIEWS:	
		A Handbook of Sugar Analysis; Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines; Textbook of Chemical Technology and Metallurgy; Die Synthese des Kautschuks; Soil Fertility and Fertilizers; Das Hydrosulfit; The Analysis of Paint and Varnish Products...	172
		NEW PUBLICATIONS.....	175
		RECENT INVENTIONS.....	176
		MARKET REPORT.....	178

EDITORIALS

COÖPERATION AMONG CHEMISTS AND MANUFACTURERS

Men in a calling which has so many ramifications as has chemistry in its various applications to all modern activities, must coöperate if the profession, as a whole, is to advance symmetrically and uniformly.

Before such coöperation can be effective, mutual understanding between the profession and the manufacturer must be achieved. It is true that many of the chemical manufacturers still follow the old rule of thumb methods without themselves having any notion of the underlying principles which are unchangeable and inexorable. These manufacturers must be brought to see the actual existence of such principles and to realize that an understanding, as well as strict compliance therewith, is necessary for the attaining of that measure of success which is necessary in order to maintain uniform quality and maximum output of finished product.

The organizers of the Eighth International Congress of Applied Chemistry, which recently met in New York, endeavored to bring about some such mutual understanding between the manufacturers on the one hand, and the educators and those who practice chemistry as a profession on the other. To this end more than two hundred chambers of commerce and eight thousand manufacturers in the United States, as well as over two hundred and fifty educational institutions were appealed to in special bulletin setting forth the points in which coöperation between these three representative divisions would be valuable and helpful. The commercial side, as represented by the chambers of commerce and manufacturers, was informed, in effect, that our educational institutions felt that the complaints, so frequently made by those engaged in commercial pursuits, of the lack of intellectual equipment possessed by young chemical graduates, were due in a large measure to the policy of secretiveness followed by our chemical manufacturers. They were appealed to to break down this policy of secrecy and to coöperate with our educational institutions, so that the record of The Eighth International Congress, as reported in its proceedings, would disclose to our foreign visitors a hearty coöperation between the educational and manufacturing institutions of our country. On the other hand, the duty of coöperation with the manufacturer was urged upon the educational institutions.

The results have shown that neither the manufacturers nor the educators responded to the suggestions of the organizers of the Congress. This is to be regretted, for it is not likely that such another opportunity will be offered in this country for fifty years or more. However, the seed has been sown; the idea and its need still exist. Let us all work together to the end that it may not be very many years before such coöperation will become an accomplished fact.

The American Chemical Society, with its membership of more than six thousand, represents to-day the

greatest, the strongest, the most active, and the most virile association of chemists in the world. It is through the members of the American Chemical Society, associated as they are in forty or more sectional units, that such coöperation seems most likely to be finally accomplished.

In New York City, the chemist who is to be appointed to the Municipal Board on Combustibles and Explosives is selected by the Mayor from among three names submitted to him for that purpose by the New York Section of the American Chemical Society. Efforts are now being made to obtain similar coöperation in other departments of the City of New York government. Chemists have coöperated in the purchasing bureau of the city, and in less than three years the savings effected by them run into tens of thousands of dollars annually.

Similar efforts at municipal coöperation are likewise successful in Boston and Philadelphia. These facts brought to your attention now may act as a seed-crystal around which your own efforts may crystallize.

The efforts made by those in charge of the Eighth International Congress of Applied Chemistry, and the New York Section of the American Chemical Society, show that making converts to the cause of cordial coöperation is a slow and laborious proceeding, particularly in chemistry, because, while the work of the chemist is fundamental and essential, that fundamental and essential character is not always obvious to the lay mind. That is the reason why, in making converts, you will meet with very meager and slow results at the start. While it may take you years to get the Government and the manufacturers to work with the chemist, the value of the result should spur you on to greater effort rather than cause you to lose heart.

Probably the broadest opportunity to raise the standard of the chemical profession in the United States, to bring about better understanding between manufacturers on the one hand and the chemists on the other, to promote acquaintance, personal, social, and otherwise among those who practice chemical pursuits, is in an institution like the Chemists' Club of New York City. While this club is located in New York City, it is not alone for the chemists of New York, but it is devoted to the interests of the chemical profession of the entire United States. It knows no state, no sectional boundary. Its field ranges over the entire domain of chemistry; those with whom it seeks to coöperate and those whom it seeks to benefit, are those of us who teach, practice, or apply chemistry anywhere in the United States. The Chemists' Club is organized on the broadest lines conceivable.

You ask what the Chemists' Club can do for those in the south and west. A chemist residing at a distance greater than twenty-five miles from the Building in New York City, and not regularly doing business in the city, is entitled to non-resident membership for \$10.00 per year. Now what do non-resident mem-

bers get for that \$10.00? The Chemists' Club has its home in the Chemists' Building, which is the only building in the world erected for the particular and peculiar benefit of the chemical profession. It has laboratories from the top floor down to the sixth; it has two floors of sleeping rooms; it has a good restaurant and a good social room; it has a good library. A non-resident member coming to New York can put up at the Chemists' Club as he would at a hotel, and if he finds that he needs a laboratory for a week or ten days or a month or six months, he can have it. The Club has three laboratories for rent to transients.

You may come to New York to sell a product or a process, and it may be necessary to make a laboratory demonstration. You cannot walk into somebody's else laboratory, and get the necessary accommodation and the necessary privacy. You may be a man without a country and a stranger without a home, but you need not be either if you are a non-resident member of the Chemists' Club. You may live, have every laboratory facility and enjoy the use of a most valuable chemical library in this building in the center of the city. You cannot do that in any other city in the world. No technical organization in any country offers so much to its non-resident members as does the Chemists' Club in New York City.

Many of you have been in a position where you have wanted a certain volume of the *Berichte*, the *Annalen*, or any one of a number of other journals or a text-book, or have wanted a translation into English of some French, German, or Italian reference. Non-resident members of the Club telegraph or write to the Club librarian and receive that particular volume by return mail; if the book is not in duplicate, transcripts will be made of the portions that you want and will be mailed to you; at the end of the month you will get your bill for services which will be made at cost since the Club is not run for profit.

Some of you may not need literature, but it is just possible that you may want some chemical that is not stocked by any of the chemical dealers in the United States. If the plans of those in charge of the Chemists' Club do not miscarry it will be only a short time when by telegraphing or writing to the Chemists' Club they will be able to take out of their museum an original package of the chemical that you want but cannot buy in the United States, and mail it to you; you in turn will order from the maker, at your convenience, an exact duplicate of the original package to replace the one loaned you by the Chemists' Club. What have you gained? You have saved the expense of a cable, consequent delay, and a fuss at the customs house. The American chemist, next to membership in the American Chemical Society, has never been offered a better opportunity for coöperation than membership in the Chemists' Club.

The development of the Club Library is an example of coöperation. Mr. Herman Frasch has most generously donated \$10,000, the income from which is to go for the purchase of new books. Prof. Chas. F. Chandler, of New York City, has donated practically all of his private library, and Prof. John W. Mallett,

of the University of Virginia, donated practically all of his library; the American Chemical Society and the New York Section of the Society of Chemical Industry have given their books; we also have the benefit of the Sir William Henry Perkin Library Fund, and the Charles Frederick Chandler Library Fund. Numerous members have donated parts or all of their working libraries, and the libraries of several of our deceased members have passed into the possession of the Club. The aim of the Chemists' Club is to get together the most complete set of books on chemical subjects in existence, and further to have as many as possible of them in duplicate, so that we may have a circulating library of immense proportions.

Those of you who are members of the Chemists' Club, or the American Chemical Society, or both, will find that the best and the most useful resting place for such of the books in your library for which you yourself have no further use, will be in the custody of the Chemists' Club.

The Chemists' Club further maintains an employment bureau for the use of chemists, whether members or not, who are out of a position; this bureau does not seek to aid those already in a position to better themselves; all it does is to give a man a start, and once he has that he must make or break himself. By notifying the employment bureau of the Chemists' Club of vacancies in your district or by sending to it names and addresses of worthy chemists who are out of positions, you will be adding greatly to the effectiveness of that bureau which has for many years past helped hundreds of men annually in obtaining good positions and in enabling many manufacturers to get suitable chemical assistance with little delay.

We have pointed out only a few of the opportunities for coöperation, and dilated upon the benefits that the Chemists' Club will confer upon the individual chemist and upon the chemical profession as a whole. The field of coöperation is too big to do more than merely to scratch the surface and commend it to your serious consideration and to solicit your earnest support.

B. C. HESSE

THE PRESENT STATE OF THE ART OF INDUSTRIAL MANAGEMENT

The American Society of Mechanical Engineers have made, through a sub-committee of that organization, a most careful study and an elaborate report on the present status of the efficiency movement in industrial work. They have carefully analyzed the problem and classified their conclusions in by far the most important contribution so far submitted on this subject. We have carefully summarized their work in the following abstract:

During the past few years a number of striking phenomena, in connection with industrial management, must have become evident even to the most superficial observer. The more important are:

(a) The wide-spread, popular interest in the subject which had its rise in a statement made before the Interstate Commerce Commission, in a hearing on the matter of proposed advances in freight rates, that by

the application of newly discovered principles of management "in the railroad operation of this country an economy of \$1,000,000 a day is possible." This popular interest is shown by the great number of articles published in the daily papers and popular magazines, mediums that give but scant attention to technical subjects except of the most striking nature.

(b) The suddenly intensified interest in the subject on the part of employers and business executives in many lines of activity, shown by lectures, addresses, professional papers and reports presented to their associations.

(c) The opposition of labor unions to the newer methods of management, shown by statements of labor leaders, in a few instances by strikes, and by an attempt to prohibit by law the use of some of these methods in Government shops.

(d) Government recognition of the matter shown by the appointment of a special committee of the House to investigate systems of management in Government arsenals and shops, which reported in March, 1912; by the appointment of a civilian board by the Secretary of the Navy to investigate management in the navy yards, which reported in July, 1911; and by a Senate bill, S 6172, now in committee, which is intended to prohibit time study and the payment of premiums or bonus on Government work.

(e) The rapidity with which literature on the subject has accumulated. One directory of books on business management lists 500 titles, and states that 75 per cent. of them have been written within five years.

(f) The formation of two societies having as an aim the furtherance of the applications of the principles of management.

(g) The separation of persons interested in the matter into two camps, one of enthusiastic advocates, the other of vigorous opponents of what is called the new element in management.

(h) The unquestionable proof of the advance that can be made in unskilled work, as shoveling material, and in ancient trades, as bricklaying, by the application of the principles of management. This is the most striking phenomenon of all.

Before defining the element in the art of management that has given rise to these phenomena, it is necessary to review briefly the beginnings of modern industry. This gives a historical setting from which the present can be more truly judged.

Modern industry was brought about by the change from handicraft to manufacture, and early British economists held that the application of the principle of *division of labor* was the basis of manufacture.

It appears, however, that another principle is the basic one in the rise of industry. It is the *transference of skill*. The transference of skill from the inventor or designer to the power-driven mechanism brought about the industrial revolution from handicraft to manufacture.

No better single illustration of the application of this principle can be found than in the invention of the lathe slide rest by Henry Maudsley, in 1794. So

complete has been this transference of skill that today hand tooling is a vanished art in American machine shops. Very few lathe hands can chase a thread with hand tools, yet all can cut good threads on an engine lathe, thanks to the slide rest.

Methods of analyzing and recording operations were early developed. Adam Smith recorded the divisions of the work of manufacturing pins, listing all operations. Charles Babbage gave a table from a French investigator showing the number of operations, time for each, cost of each, and expense of tools and material for making pins in France in 1760.

Thus we see the application of the principle of *transference of skill* at the basis of the development of the industry, and an early application of the value of the detailed study of operations in making that transference more complete. But the machine was the viewpoint. It was looked upon as the producing unit. The subsequent development has had the effect of advancing still further the division of labor, and beginning the division of thought. The drafting room presents the first example of this trend, in its collection of engineering data, in its prediction of results and the formation of staff organization. The art of machine design has been greatly developed. The last half of the last century saw a tremendous increase in inventions, a tremendous furtherance of the application of transference of skill to machine and tools. The skeleton of an industrial organization of this period, one that was too large for a single executive to manage, consisted of a designing department and a production department, each with a head responsible to the manager.

The first of these, the one that was the means of embodying skill in the machinery and tools of production, was highly developed and organized. Experiment, research and detailed study were constantly resorted to, to aid in reaching the desired result. The work was highly specialized and the employees highly paid. Not infrequently the manager or chief executive devoted much of his own time to this part of the business.

The production department presented a contrasting condition. The workmen were given the tools and machines designed in the drawing-room and using their own unaided skill were expected to produce work of the desired quality and quantity. Except in rare instances, no effort was made to transfer the skill of the management to the production department and to the employees, or to undertake the division of executive thought. Very little consideration was given to the workmen as a producing unit.

Within the past 20 or 25 years certain changes have taken place in the attitude of many production managers toward the problems that they face and the forces and means that they control. An early evidence was the development of profit-sharing, premium and bonus systems to reward increased effort and output. There followed welfare work, industrial betterment movements, the adoption of safeguards and regulations to minimize industrial accidents, the substitution of the principle of accident compensation for

employers' liability and an improvement in the physical surroundings and conditions of factories. All of these tendencies have been fostered and to a great extent initiated by employers. But even today these are by no means generally adopted.

Another tendency, less pronounced in character, has as its object the improvement of the personal relations between the employees themselves and between the employee and the employer. It is the effort to establish the best of factory working conditions in those things not physical in nature, to develop and maintain a shop atmosphere free from all harassing and hindering influences. It is an attempt to make use of the results of experimental psychology in improving working conditions.

But the most important change and one that comprehends the others, is in the mental attitude toward the problems of production. The tendency is toward an attitude of questioning, of research, of careful investigation of everything affecting the problems in hand, of seeking for exact knowledge and then shaping action on the discovered facts. It has developed the use of time study and motion study as instruments for investigation, and the planning department as an agency to put into practice the conclusions drawn from the results of research, and methods of wage payment which stimulate cooperation.

All of these changes have affected the production department much more than the designing department. The effect is to extend the principle of trans-

ference of skill to production, so that it completely embraces every activity in manufacture. The skill of management is consciously transferred to all of the operations of the factory. This extension is expressed by these phases; the drawing-room is the planning department of design, and the planning department is the drawing-room of production.

To obtain information on present conditions, the committee wrote to the recognized experts, to executives of plants in many lines of industry, to students of industrial problems, and it has had many interviews with men in these various fields. The responses to the requests were in the main most generous, and the replies convey the ideas of a conscious effort to ascertain and study facts and systematically to apply them to instructing the workmen and in controlling every department of industry. Setting these against the underlying principle of the transference of skill, they conceive the prominent element in present-day industrial management to be: *the mental attitude that consciously applies the transference of skill to all the activities of industry.*

Here emphasis is placed upon the word *all*, for the restricted application of this principle to machines and tools has been highly developed for a long period. But its conscious application in a broad way to the production departments, and particularly to the workmen, we believe has been made during the last quarter century.

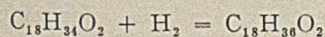
ORIGINAL PAPERS

THE HYDROGENATION OF OILS¹

By CARLETON ELLIS

The treatment of unsaturated oily bodies with hydrogen to obtain saturated derivatives is of great scientific and technical interest. In the fat industry a most fascinating problem has been that of the conversion of oleic acid or olein into stearic acid or the corresponding glyceride.

Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:



Thus 282 pounds of oleic acid require 2 pounds (or about 0.7 per cent.) of hydrogen for the production of 284 pounds of stearic acid, and similarly the transformation of olein into stearine requires the use of about 0.68 per cent. hydrogen.

One thousand cubic feet of hydrogen weigh approximately 5.6 pounds, hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cubic feet of hydrogen per ton (of 2000 pounds) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.

Many attempts to hydrogenate oleic acid have been

made. Reviewing this subject in 1897¹ Lewkowitsch refers to the ease with which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

Prior to this, however, Goldschmidt, in 1875,² had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200-210° C. This presumably led to the attempted commercial development of a process by de Wilde and Reyckler³ involving heating oleic acid to 280° C. with 1 per cent. of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent. of the theoretical. Only about two-thirds of the iodine could be recovered so the process apparently did not find technical use.⁴ Should the much lauded method of treating kelp, primarily for obtaining potash salts, come into use, a cheap supply of iodine

¹ *J. S. C. I.*, 389 (1897).

² *Sitz. b. d. Wiener Akad. d. Wiss.*, 72, 366.

³ *Bull. Soc. Chim.*, [3] 1, 295 (1889).

⁴ *Chem. Ztg.*, 1889, 595.

would be available which might then make the Wilde and Reychler process of some technical interest.

Chlorine in lieu of iodine has been tried, but great difficulty has been experienced in securing an autoclave of resistant material. Imbert¹ recommends using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and pressure of about five atmospheres for a period of six hours.

Zürrer² chlorinates the fatty acid and then heats with water in the presence of a finely divided metal as zinc or iron. Lewkowitsch alleges that the treatment of monochlor-stearic acid in this manner causes a reversion to oleic acid.

Tissier, in 1897,³ lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein introduced and treated under pressure.

Under the circumstances the glyceride is hydrolyzed to fatty acid and glycerine, and according to Tissier nascent hydrogen is evolved by virtue of the finely divided metal and reduces the oleic to stearic acid. Freundlich and Rosauer⁴ claim the Tissier process to be inoperative.

The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the Varentrapp reaction⁵ has not proved to be of much commercial significance, although it appears that certain firms have been making use of the process in a limited way.

The Schmidt zinc chloride process⁶ involves heating oleic acid and zinc chloride at exactly 185° C. while interaction is taking place. "Deviation from this point leads to an increase of liquid substance. Unfortunately the solid candle material must be distilled and the considerable proportion of β -hydroxystearic acid (melting point 82° C.) in the crude product is seriously diminished by the partial conversion of this acid into oleic and iso-oleic acids. Thus, from a candle-maker's point of view, a substance of high melting point is rendered practically valueless. Schmidt's process was tried on the large scale in an Austrian candle works. The quantity of liquid *unsaponifiable* substance obtained was, however, so large that commercial success was out of the question."

Many processes have been proposed based on the well-known action of sulfuric acid on oleic acid. Hydroxy-stearic acid is obtained by steaming the product. It would lead us too far from the present subject to enter into any further discussion of these reactions.

PROCESSES INVOLVING APPLICATION OF ELECTRICITY

In 1886, Weineck⁷ called attention to the possibility of electrolytic addition of hydrogen to oleic

acid. Kuess¹ later attempted to apply the electric current in the steam distillation of fatty acids.

In patents taken out by Magnier, Bragnier and Tissier,² the fatty material is acidified with sulfuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atmospheres is subjected to the action of an electric current, which generates hydrogen in a nascent state.

An interesting method of converting oleic into stearic acid is that comprised in the Hemptinne electric discharge process. The method is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil.³

Fig. 1 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe, H, furnishing hydrogen under constant pressure. Oleic acid is supplied by a pipe, O, to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass

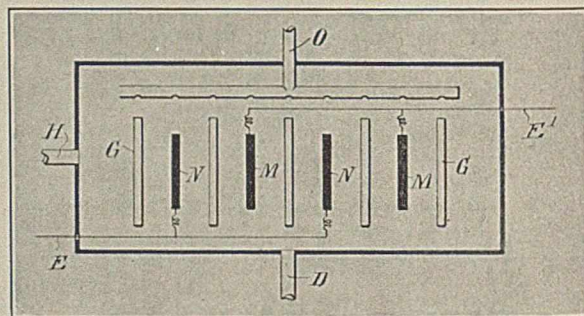


FIG. 1

plates G and alternately the metal plates M, N. The metal plates M are connected to one pole, the others, N, being connected with the other pole of a source of electricity. As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting points in the neighborhood of 69° C.

Hemptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent. of stearic acid. Repeated treatment permits even up to about 40 per cent. yield. Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by saturating to the extent of about 20 per cent., removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent. yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent. of the total weight. It is stated that the presence of these bodies

¹ U. S. Patent No. 901,905, of Oct. 20, 1908; see also *Bull. Soc. Chim.*, 1899, 695, 707.

² German Patent No. 62,407, of Aug. 8, 1891.

³ French Patent No. 263,158, of Jan. 16, 1897.

⁴ *Chem. Ztg.*, 1900, 566.

⁵ *J. S. C. I.*, 98 (1883), 200 (1884).

⁶ Lewkowitsch, "Oils, Fats and Waxes," p. 664.

⁷ *Osterr. Privil.*, 10, 400 (July 19, 1886).

¹ *Chem. Ztg.*, 1896, 618.

² Eng. Patent No. 3,363, 1900; German Patent No. 126,446, of Oct. 3, 1899, and additional German Patent No. 132,223.

³ U. S. Patent No. 797,112, of Aug. 15, 1905.

does not impair the market value of what some one has termed "electrocuted" oleic acid.

"J. Petersen¹ also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulfuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent."

Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

C. F. Böhringer and Sohne² obtained by the same method much better results when using as cathodes, metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes are not as effective.

Kolbe³ in 1871 states that Saytzeff reduced nitrobenzol to aniline by passing the vapors of the former, mingled with hydrogen, over palladium-black.

About twenty-five years later Sabatier and Senderens began their classic study of nickel and other metallic catalyzers.

The work of Sabatier and Senderens laid the foundation for the present processes of hydrogenation of oils. Their work is so well known that it is needless to discuss it here.

Fig. 2 shows apparatus used by these investigators in the hydrogenation of bodies capable of vaporization. In this apparatus, 1 is a hydrogen generator; 2 and 3 are wash bottles and 4 is a vaporizer containing

the matter have, moreover, been subjected to a great deal of scrutiny because of the alleged basic character of certain of them. For these reasons the following discussion pertains very largely to processes which have been covered by patents in this country or abroad.

(NOTE.—The illustrations herein are largely derived from the drawings of patent records or have been prepared from written descriptions. All details deemed unnecessary in the portrayal of the essential features of these processes have been omitted. The original records should, of course, be consulted for details.—AUTHOR.)

A German Patent, No. 139,457, of July 26, 1901, to J. B. Senderens, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyzers. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron, or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

The first disclosure of the possibility of hydrogenation of oils in a liquid state apparently comes from Le Prince and Siveke.¹ In England a corresponding patent (No. 1515, of 1903) was issued to Normann² and the latter patent has become widely known because of its alleged fundamental character.

Normann states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 3

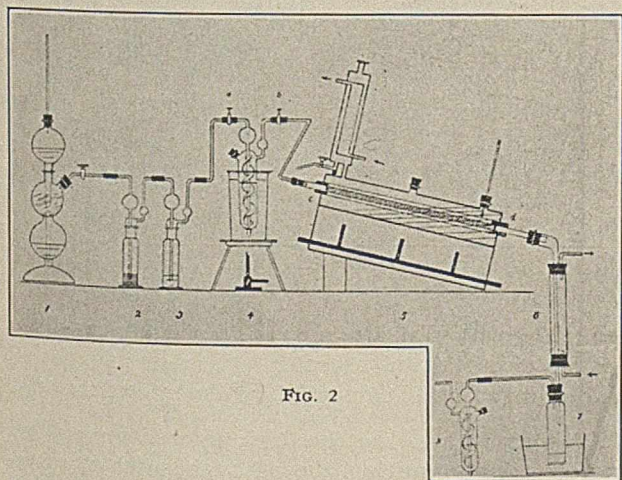


FIG. 2

the substance to be converted into a vapor. 5 is a hydrogen chamber containing nickel catalyzer and heated by an oil bath. 6 is a condenser.

While a good deal of work has been done on the hydrogenation of fatty oils, the literature on the subject is very meagre indeed and only through the patents which have been issued can we gather from any published records much that is enlightening as to developments in this industry. The patents concerned with

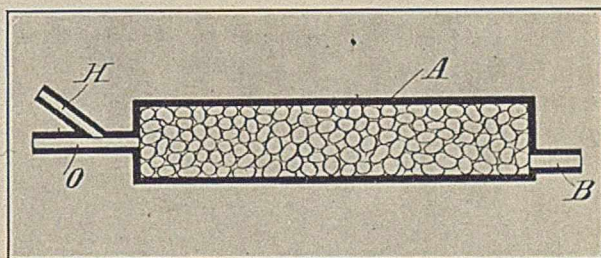


FIG. 3

in which A is a bed containing granular pumice coated with a metal catalyzer. O is an inlet for oil vapors and H is an inlet for hydrogen. The mixture passes through the tube A and the converted material is withdrawn at B. Normann notes, however, that it is sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. He states, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current

¹ German Patent No. 141,029, of Aug. 14, 1902, Herforder Maschinen-fett und Oel Fabrik.

² This English Patent is owned by a large soap manufacturing house in England and it is reported they allege the patent in that country to be fundamental and controlling for the hydrogenation of fatty oils generally. They are offering rewards for information as to the secret and unauthorized use of the process and it is said already to have started litigation.

¹ Z. Elektrochemie, 1905, 549.

² Ger. Patents Nos. 187,788, 189,332, 1906.

³ J. prakt. Chem., [2] 4, 418 (1871).

of hydrogen caused to pass through it for a considerable time, that the oleic acid may be completely converted into stearic acid.

Fig. 4 shows very simple apparatus, such as might have been used by Normann to this end. A is a vessel containing oil, O, in which fine particles of nickel are

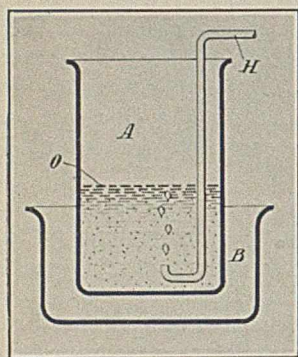


FIG. 4

suspended while a strong current of hydrogen from the pipe H affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow having an iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about

10 and a melting point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen.

The disclosures of the Normann patent are, however, rather meagre and hardly can be considered to comprehensively traverse the difficulties encountered in the practical hydrogenation of oils in a liquid state. Dr. David T. Day, of Washington, has brought out a process¹ in which he treats, not fatty oils, but hydrocarbon oils, with hydrogen in the presence of what he terms a porous absorptive substance, mentioning palladium-black, platinum sponge, zinc dust, fuller's earth and other clays. Fig. 5 shows one method proposed by Day to this end.

The upper chamber A is filled with hydrocarbon oil, and porous absorptive material such as palladium-black is introduced in the intermediate chamber C

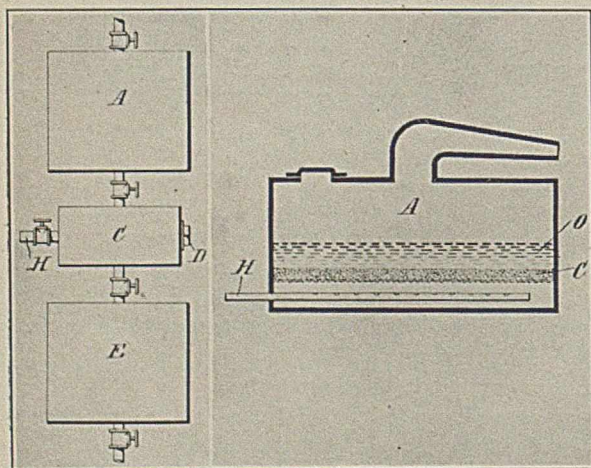


FIG. 5

FIG. 6

by way of the plugged orifice D. Any air present in C may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe H until the porous material has absorbed

its full quota. The hydrogen gas may be admitted under a pressure of 100 pounds or more to the square inch. When the porous material in C has become properly charged with hydrogen, the oil is allowed to run from the chamber A through the chamber C into the collecting chamber E, hydrogen being introduced as required by the pipe H.

In the place of hydrogen, Day states that ethylene or other hydrogen carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oil is in great part removed and the burning qualities of the oil improved. When palladium black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

Fig. 6 shows a modification of Day's process. A is an oil still, in the lower part of which the perforated pipe H serves for the admission of hydrogen. Palladium-black or other porous absorptive material forms a layer, C, on a screen above the hydrogen inlet. O shows the charge of oil. In operating this apparatus the layer of material C is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.

A peculiar manner of treatment has been shown by Schwoerer,¹ which will be made clear by Fig. 7. The receptacle A, which is heated by the steam jacket S, is provided with what Schwoerer calls a helical

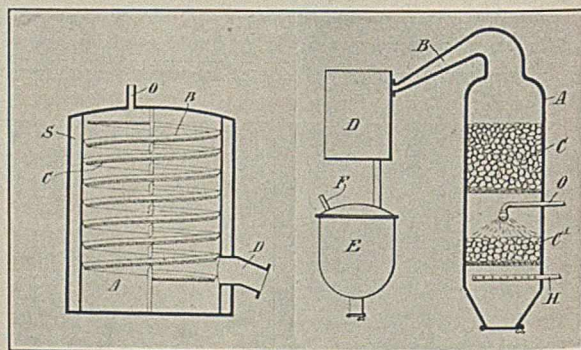


FIG. 7

FIG. 8

pan, shown at B. The underside of the pan carries a layer of nickelized asbestos. O is an inlet for oil and hydrogen, and D an outlet for the treated material.

Schwoerer states that he first mixes fatty acid and hydrogen by atomizing the oil with a jet of superheated steam in the presence of hydrogen and conducts this mixture through the pipe O, into the chamber A. The temperature maintained in the apparatus is from 250 to 270° C. Vapors of oleic acid come in contact with the layer of catalyzer on the underside of the helical pan and are converted into stearic acid. The product collects, more or less, in the gutter of the helical pan and is removed at D.

The repeated caution given by Sabatier to bring in contact with the catalyzer only the vapors of the

¹ U. S. Patent No. 826,089, of July 17, 1906.

¹ U. S. Patent No. 902,177, of Oct. 27, 1908.

material, doubtless led Schwoerer to devise this form of apparatus.¹

Bedford, presumably with the same caution of Sabatier in mind, discloses, in U. S. Patent No. 949,954, of Feb. 22, 1910, a process which also has to do with vaporization of the oily material. Fig. 8 shows the Bedford apparatus. A still or tower, A, carries two beds of catalyzer, C and C'. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed from the pipe O, onto the catalyzer bed C'. Hydrogen is admitted through the pipe H. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained in the still or tower A. The vapors of oleic acid mingled with hydrogen pass through the second catalyzer bed C, where more or less conversion occurs, then pass to the condenser D, and finally collect in the receptacle E. F is a connection to a vacuum pump.

Neither this process nor that of Schwoerer is broadly applicable to the treatment of glycerides as these cannot be vaporized without undue decomposition.

Erdmann has taken out a German Patent No. 211,669, of Jan. 19, 1907, involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like. Fig. 9 probably indicates one form suggested by Erdmann, who, by the way, does not show any drawings in the

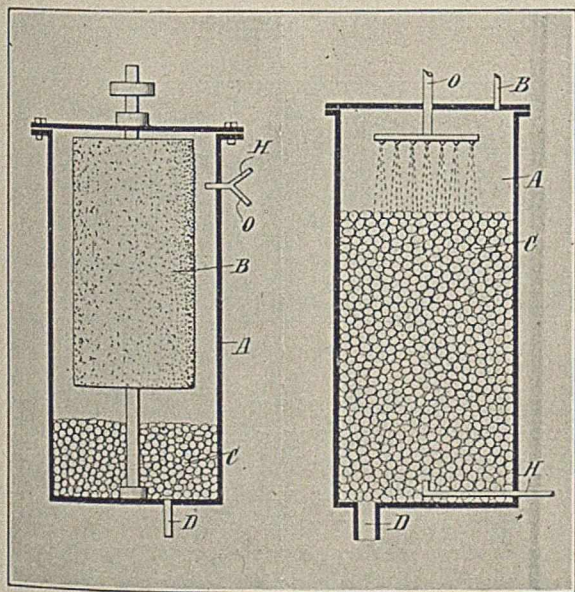


FIG. 9

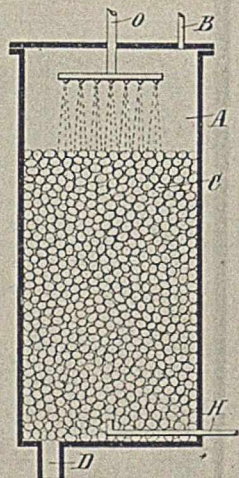


FIG. 10

tating cylinder B, then passes through the bed C, the oil being drawn off at D. The excess of hydrogen is presumably vented in the upper part of the apparatus.

A second modification (Fig. 10) involves a tower, A, filled with catalyzer C, which may be in the form of nickel supported on coarse fragments of pumice. By the pipe O, oil is admitted to the chamber in an atomized or finely divided state. Hydrogen enters by the pipe H. Erdmann states that the temperature of treatment should be from 170 to 180° C. The treated oil is drawn off at D while the excess of hydrogen passes away at B.

In a supplemental patent, No. 221,890, of Jan. 19, 1907, Erdmann recommends the steam distillation from the reaction chamber of the saturated product under diminished pressure.

Vereinigte Chemische Werke A. G.² make use of palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that one part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of two to three atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide and sulfide, liquid hydrocarbons and carbon bisulfide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

Kayser² describes a process of treating oil with metallic catalyzer consisting in mechanically agitating the oil and catalyzer in the presence of hydrogen, preferably under pressure. One form of the apparatus indicated by Kayser for this purpose is diagrammatically represented by Fig. 11.

Here A is a closed horizontal cylindrical vessel in which is a paddle wheel, D, made up of blades carrying wire gauze. The paddle wheel is rotated

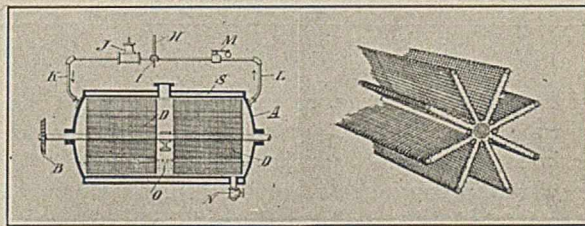


FIG. 11

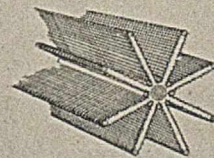


FIG. 12

patent. The chamber A has a rotatable cylinder, B, which is coated with nickel catalyzer. In the bottom of the receptacle is a quantity of nickelized pumice. Oil enters at O and is atomized by hydrogen entering at H. The atomized mixture impinges upon the ro-

¹ Salatiel and Senderens, *Annales de Chimie et de Physique*, [8] 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou à la suite d'un abaissement accidentel de la température du tube." They further say that in the preparation of cyclohexanol and its homologues from phenol or cresol at a temperature but slightly above the boiling points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

by a driving gear at B. In the upper part of the tank is an inlet for charging oil and presumably also catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at H and passes, by the three-way cock I, to the compression pump J, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe, L, carrying a blow-off valve, M, for the

² German Patent No. 236,488, of Aug. 6, 1910; also English Patent No. 18,642, of 1911.

² U. S. Patent No. 1,004,035, of Sept. 26, 1911.

purpose of venting the unabsorbed hydrogen. The temperature of treatment is stated to be about 150 to 160° C. Although the claims call for the use of hydrogen under pressure, no working pressures are specified. Fig. 12 shows diagrammatically one form of construction of the screen-covered paddle wheel used by Kayser.

In another U. S. Patent (No. 1,008,474, of Nov. 14, 1911), Kayser sets forth the use of an inert pulverulent material such as kieselguhr as a carrier for the nickel catalyzer, he apparently having determined, as did Sabatier and others, that hydrogenation is more rapid or complete when a carrier for the catalyzer is used; and he claims the process of hydrogenating oil involving agitation of a metallized inert pulverulent carrier with a fatty oil in the presence of hydrogen. It is commonly understood that the Kayser process is in operation on the large scale in this country.

Two patents relating to the spraying of oil into a chamber containing compressed hydrogen have attracted some attention abroad. One of these is English Patent No. 7,726, of 1910, to Testrup and the other is to Wilbuschewitch which finds its counterpart here in U. S. Patent No. 1,024,758, of April 30, 1912. Fig. 13 shows the elements of the Testrup process.

Oil and catalyzer are pumped through the pipe O, into the tank A, and hydrogen is admitted by the

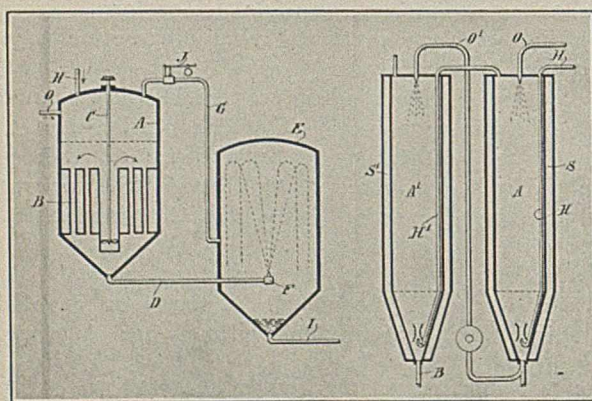


FIG. 13

FIG. 14

pipe H, to furnish a gas pressure of say 15 atmospheres. The tubes B are heated by steam and the stirrer C circulates the oil and catalyzer in the tank A, until the oil has become heated and presumably somewhat hydrogenated. The oil is allowed to pass into the adjacent tank E, entering this tank by the spray nozzle F. Hydrogen gas is admitted to the tank E, from the tank A, so as to afford a pressure of, say, 12 atmospheres in the tank E. A series of tanks may be arranged with a constantly decreasing pressure so that the differential pressure enables the spraying of the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50.

As catalyzer, Testrup recommends finely divided palladium or preferably nickel, the latter being two to three per cent. by weight of the oil. As a

treating temperature 160 to 170° C. is mentioned.

The Wilbuschewitch patent itself details a rather complicated system and Fig. 14 shows only what appears to be the essential features of the treating apparatus. Several tanks or autoclaves are connected as shown at A and A', oil entering the top of the tank A by the pipe O, to form a spray which in descending meets an upward current of hydrogen entering by the pipe H. The oil is drawn off through the pipe O', and sprayed into the tank A'. This time it meets a current of hydrogen represented by the excess of hydrogen coming from the tank A. The treated oil is drawn off and may be centrifuged to remove the catalyzer. A pressure of nine atmospheres is recommended and the pressures may be varied in the different tanks.

Of the Wilbuschewitch process Goldschmidt¹ states that the high hydrogen pressures employed enable the reaction to take place quickly at temperatures between 100 and 160° C., so that the fat is not likely to be injured by the temperature to which it is subjected. It should be stated that several years previous to the date of the Wilbuschewitch patent, Ipatiew had noted and carefully studied the action of increased pressure.²

Bedford and Williams³ have brought out an interesting process represented by U. S. Patent No. 1,026,339, of May 14, 1912. Fig. 15 shows the apparatus indicated by Bedford and Williams for carrying out the process. Oil is placed in the receptacle A,

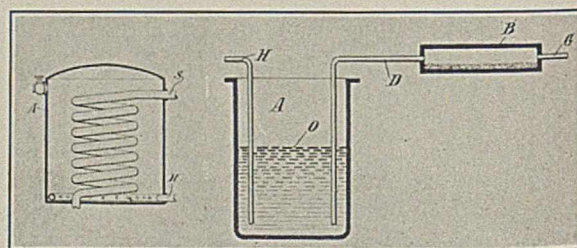


FIG. 15

FIG. 16

which is heated by a steam coil, S. Metallic oxide catalyzer is added, about 1 percent. being recommended, and hydrogen and oxygen or air is introduced by the pipe H. As a catalyzer, nickel oxide (previously used by Ipatiew) is recommended and instead of the customary hydrogenating temperature of 150 to 170° C., a temperature of about 250° C. is employed. While hydrogen alone may be used for the purpose, the inventors recommend and claim treatment of the oil

¹ Chem. Ztg., 1912, 945.

² Rumor has it that the processes of Testrup and Wilbuschewitch were so much alike that during the prosecution of their patent applications before the English Patent Office, they concluded to unite interests and that subsequently they sold the rights in England to a soap manufacturer who, it is alleged, proposes to contest the claims of the present owners of the Normann patent as to the alleged basic nature of the latter.

³ It is reported that in England some of the independent soap manufacturers have taken over this patent of Bedford and Williams and also the Erdmann rights. The Bedford and Williams process does not seem destined to be of great service in connection with the manufacture of edible fats, in part owing to the high temperature employed. It is questionable whether or not working with a mixture of hydrogen and oxygen in the presence of a catalyzer might not at times afford conditions leading to explosions.

with a mixture of hydrogen and oxygen to form hydroxy fatty acids or their glycerides.

Shukoff¹ claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. Nickel carbonyl may be obtained from reduced metallic nickel by passing carbon monoxide over it at a low temperature. Nickel carbonyl is soluble in oil and is very readily taken up by gases. On heating to a temperature of 200° or so, the carbonyl is decomposed setting free, in a nascent state, metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by the method indicated by Fig. 16. Carbon monoxide is passed by the pipe G, into the tube B, containing finely divided nickel and the nickel carbonyl formed is conducted to the oil O, which is heated to about 180°. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220 or 240° C. and hydrogen gas introduced by the pipe H, to bring about hydrogenation.

Day has taken out U. S. Patent No. 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen while being superheated by exterior contact of the tubes with boiling oil.

An English Patent, No. 23,997, of 1909, to Phillips and Bultell, claims to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis, or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.

The firm of H. Schlinck & Co., of Hamburg, Germany,² hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining of palladium catalyzer which offers a frictional resistance to the passage of the oil. Fig. 17 shows a centrifugal drum, *a*, which is closed at the top and can be heated. Oil and hydrogen are introduced through the pipe *b*. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series through which the oil may be caused to progress until sufficiently hydrogenated.

Ellis³ uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction. Fig. 18 shows a three-section apparatus with the catalyzer tubes T, T¹ and T², heated by the jackets S S. Oil from tank O flows through the apparatus while hydrogen, admitted by

the pipe H, passes through in an opposite direction. The arrangement permits of differential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydro-

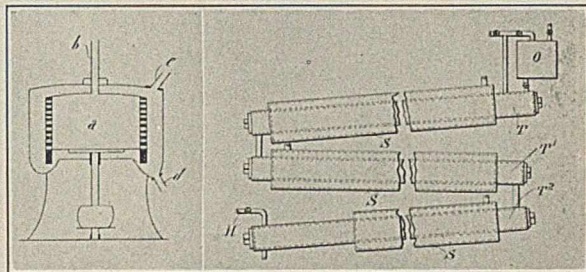


FIG. 17

FIG. 18

genation at any given point, enabling a hydrogenated product free from burnt odor to be obtained. Fig. 19 shows a vertical form of apparatus, the catalyzer being shown at C in the tube A. Oil is introduced by the pipe O, and passes into the tube or cylinder A. The pump P causes oil to circulate from the top to the bottom of the apparatus through the pipe B. Hydrogen gas admitted at H is pumped into the bottom of the cylinder A, and the excess is withdrawn at the top by the pipe D, passing through the drier E, and back into the treating cylinder. Oil may be continuously fed through the pipe O, in the upper part and the treated product withdrawn at the same rate at the lower part of the apparatus.

In Ellis' Patent, No. 1,040,531, of Oct. 8, 1912, the catalyzer is placed in trays or baskets as shown by

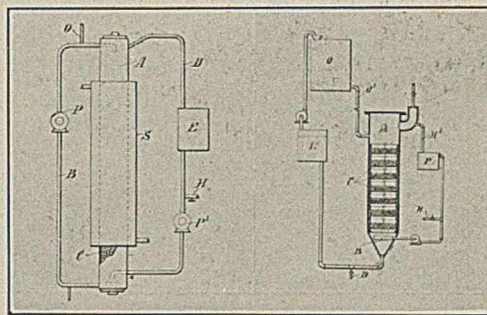


FIG. 19

FIG. 20

Fig. 20 at C. The oil travels in a cyclic path downwardly through several layers of catalyzer, and hydrogen gas passes in an opposite direction. Separation of the catalyzer in layers in this manner enables the hydrogen to pass more uniformly through the catalyzer bed. If the catalyzer forms a bed of considerable depth and width, the gas in taking the path of least resistance is liable not to come in contact with some parts of the bed.

The activity of a properly made catalyzer is oftentimes surprising. In the case of a stationary catalyzer we have noted instances of hydrogenation where oil is converted into a hardened fat by momentary contact with the catalyzer.

Fig. 21 shows a photograph of a small laboratory apparatus for testing catalyzer consisting of an in-

¹ German Patent No. 241,823, of Jan. 18, 1910. See also H. Kamps, Belgian Patent No. 246,975, *Seifensieder Ztg.*, 1912, 1339.

² English Patent No. 8,147, of 1911.

³ U. S. Patent No. 1,026,156, of May 14, 1912.

clined tube containing catalyzer and carried in a heating jacket. Oil is admitted at the right and

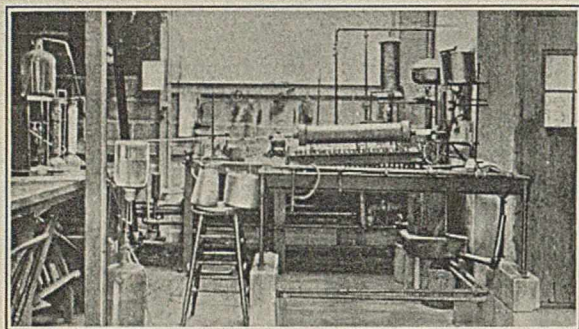


FIG. 21

hydrogen at the left hand end. Fig. 22 shows the catalyzer tube at the right from which extends a horizontal tube supplying hydrogen to the catalyzer tube.

Recently when using a new type of catalyzer we started to pass oil through the catalyzer tube and found hydrogen to be absorbed so vigorously by the oil that instead of passing off through an oil seal at

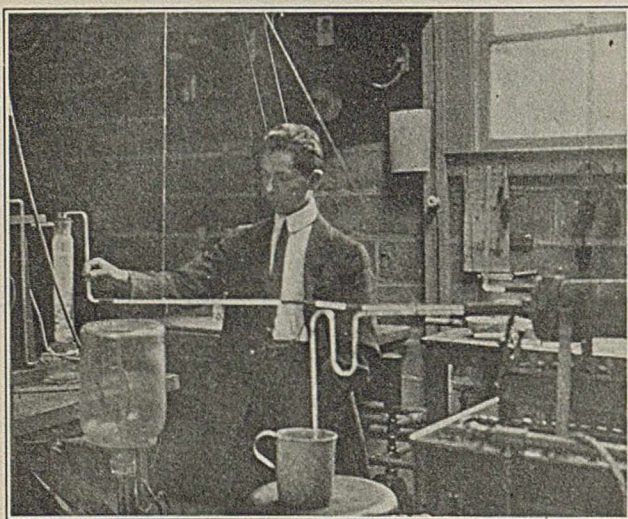


FIG. 22

the lower end of the inclined catalyzer tube, the oil, curiously enough, was impelled against the strong current of hydrogen passing through the horizontal tube, rushing through it to the point indicated by the hand of the operator (Fig. 22) and there solidifying, actually being well hydrogenated from its momentary passage through the apparatus. A peculiar feature was the advance of the oil from the tube containing catalyzer far into the tube through which only the hydrogen was entering the apparatus. The travel of the oil along the hydrogen supplying pipe in opposition to a rapid current of hydrogen, indicates the possibility of hydrogenating in a very short time, provided a catalyzer of a high degree of activity is secured.

On the other hand, some catalyzers of the nickel and cobalt type when first brought into contact with oil and hydrogen show for a time a marked degree of

sluggishness, but after a period, usually ranging from one to three hours, their activity rather suddenly augments and thenceforth remains apparent for a long period. This sluggishness should not be confounded with the seeming initial inactivity in the hydrogenation of oils containing considerable linolein or other highly unsaturated bodies. In such cases the rate of "hardening" (increase in melting point) is slow at first and later progresses more rapidly. Hydrogenation, in some cases at least, apparently proceeds selectively with initial formation of olein from linolein. Later the olein is transformed into stearin with the observed more rapid increase of titer.

Ellis' effects a constant circulation and contact of the hydrogen gas in accordance with the method shown by Fig. 23. The tank A contains a body of oil, O, the space above the oil being filled with hydrogen

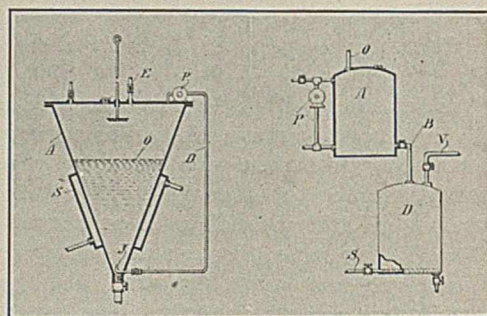


FIG. 23

FIG. 24

under any suitable pressure. The tank is heated by the jacket S. A pump, P, withdraws the hydrogen from the upper part of the tank and impels it through the pipe D, into the lower part of the tank. Catalyzer is added to the oil when the proper temperature is reached and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the roasting elements. After the operation is completed, the porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil.

In U. S. Patent No. 1,043,912, Ellis hydrogenates oil (Fig. 24) in the autoclave A. The pump P circulates hydrogen gas through the oil. The treated product is run into the deodorizer D, where it is treated with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200 to 300° C. and a vacuum of down to one or two inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum "pulled" may be considerably less.²

Contrary to the opinion entertained by many it

¹ U. S. Patent No. 1,040,532, of Oct. 8, 1912.

² See also U. S. Patents Nos. 1,037,881, 1,038,545, and 1,047,013.

does not appear needful to agitate the catalyzer primarily for the purpose of contacting it with hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed just as rapidly, simply by diffusion.

CATALYZERS

Catalyzers, those bodies which modify reaction velocity without stoichiometrical participation in the reaction, are destined to find another important industrial application in the hardening of oils.

The previous illustrations show the variety of methods proposed for mingling oil, hydrogen and catalyzer. Among these are several of excellent efficiency. But, after all, the virility, so to speak, of the process, depends on the *catalyzer*. With a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure; almost, it sometimes seems, independent of the nature of the hydrogenating apparatus.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent. Nickel oxide, as stated, has been employed by Bedford and Ipatiew. Wimmer recommends organic salts of nickel such as the formate, acetate or lactate.

As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from say a nickel sulfate solution by the addition of an alkali. Obtained in this or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably, and hydrogen gas is passed over the mass at a temperature ranging from 250 to 500° C. or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete even after long duration of exposure to hydrogen. A temperature of 300 to 325° C. gives fairly complete reduction and is a satisfactory working temperature. The lower the temperature at which the nickel is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity.

Nickel is easily poisoned by chlorine and by sulfur in the sulfide form. We have had no unfavorable results from the use of hydrogen gas passed through

a wash bottle containing concentrated sulfuric acid and then conveyed directly to the catalyzer and oil. Traces of the acid were entrained by the gas, but the catalyzer remained in active condition during about two weeks usage under these conditions.

Copper is much less sensitive to poisons than nickel, but on the other hand it is much less active.

Catalyzer made from the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers, ranging from pumice stone and kieselguhr to charcoal and sawdust.

After reduction of nickel, as above, it should be kept out of contact with air as it is extremely pyrophoric and quickly loses its efficiency on exposure to the air. Consequently when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen; also it is well to heat the oil and bubble hydrogen through it for a short time prior to the introduction of the catalyzer.

Several methods of producing catalyzers have been the subjects of the patents¹ as, for example, that of Crossfield¹ in accordance with which kieselguhr, asbestos and the like is impregnated with a solution of nickel sulfate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used the powder should contain about 30 per cent. of metallic nickel.

A similar procedure is the subject of a patent to Kayser.² In this case, however, the nickel sulfate or other nickel salt in concentrated solution may be used in an amount to saturate kieselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

Seeking to overcome the disadvantage of ready oxidation in the air possessed by normal catalytic nickel, Kayser³ reduces the nickel oxide or equivalent material at a temperature of 500 to 600° C. and then passes through the reduced material a brisk current of carbonic acid until the escaping gas proves no longer inflammable. By this method it is claimed that a catalyzer is secured which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy.

Wilbuschewitch⁴ proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotary drum. The temperature during the treatment is stated to be 500° C. Wilbuschewitch⁵ has patented a process of regenerating spent catalysts of the nickel type involving extraction with benzine, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing.

As a catalyzer in this field palladium has received

¹ English Patent No. 30,282, of 1910.

² U. S. Patent No. 1,004,034, of Sept. 26, 1911.

³ U. S. Patent No. 1,001,279, of Aug. 22, 1911.

⁴ U. S. Patent No. 1,016,864.

⁵ 1,022,347, of April 2, 1912.

considerable study, for, in spite of high first cost, its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperatures, makes it particularly attractive.

Many years ago, Fokin¹ stated he regarded palladium as the most powerful of all catalyzers, he having found that the reduction takes place readily at 80 to 90° C., while with nickel, a temperature of 180 to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while *palladium*-black would reduce oleic acid completely to stearic acid, that *platinum*-black under the same conditions gave only 24 per cent. of stearic acid.

Paal² worked with colloidal palladium preparations and hydrogenated castor, olive, fish oil and animal fats. He found that sesame oil, after hydrogenation, showed the Baudoin reaction only very faintly, while cottonseed oil no longer responded to the Becchi and Halphen reaction.³ Skita has worked with palladium incorporated with a protective colloid.

Karl⁴ has studied, with considerable care and in a quantitative way, the action of palladium supported on various bodies. He found that palladium precipitated on finely divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron, or zinc, little or no hydrogenation was effected, owing to the anti-catalytic action of these metals. While metallic zinc is anti-catalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.

HYDROGEN

One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late and undoubtedly this will lead to improvement in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron sponge steam process and the electrolytic method.

For very large plants the iron sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1,000 cubic feet of hydrogen, or less, per hour.

Lane's process is based upon the passage of steam over reduced iron and involves the generation of water gas to reduce and heat the iron oxide employed. For each cubic foot of hydrogen produced, about three cubic feet of water gas are required. The water gas has to be freed from sulfur as otherwise the hydrogen would take up sulfur from the iron sponge and poison the catalyzer. This requires the purification of three volumes of water gas, from which, as stated, a yield of only one volume of hydrogen is obtained.

¹ *Chem. Ztg.*, [2] 1906, 758; [1] 1907, 324.

² *Ber.*, 41, 2282.

³ Paal recommends (U. S. Patent No. 1,023,753, of April 16, 1912) platinum or palladium chloride admixed with a neutralizing agent such as sodium carbonate.

⁴ Inaugural Dissertation, Erlangen, 1911.

The cost of hydrogen made in this manner is about one dollar per 1,000 cubic feet. Fig. 25 shows the process as now installed in the works of a large soap

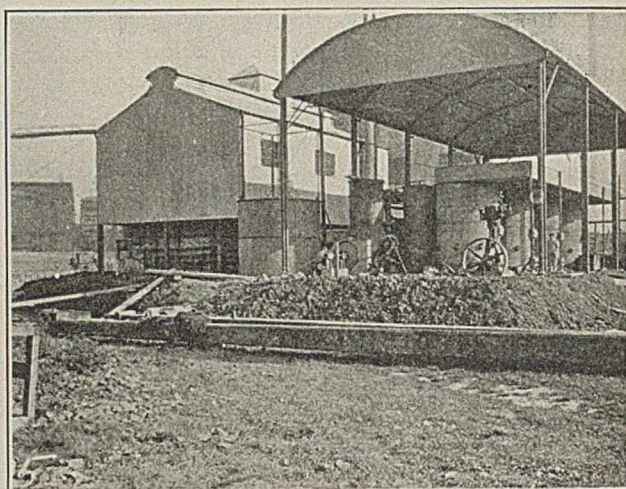


FIG. 25

manufacturer in England. Figs. 26 and 27 show the Lane process installed at a plant near Paris.

A plant of this type, having a capacity of about 5,000 cubic feet per hour, costs in the neighborhood of \$40,000.

In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil. To-day a good portion of this hydrogen is allowed to go to waste. Eventually it may be used, to some extent at least, for hydrogenation purposes.

Generators for the production of hydrogen and oxygen by the electrolysis of water are furnished by the International Oxygen Co. One type has an out-

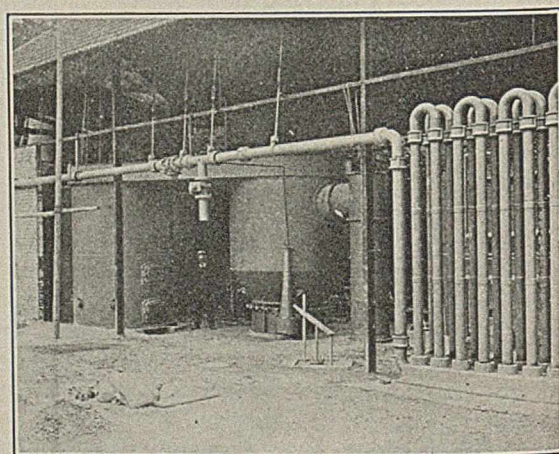


FIG. 26

put of at least 130 cubic feet of hydrogen and 65 cubic feet of oxygen, per day, giving about 7 cubic feet of hydrogen per kilowatt hour. At two cents a kilowatt the hydrogen costs about one-fourth of a cent per cubic foot, if one disregards the value of the evolved oxygen.

The electrolytic process is simple and clean and

is to be recommended, especially for plants of moderate requirements.

We have for some time used hydrogen gas derived in this way and find it suitable for hydrogenation purposes without resorting to any extensive purification.

Abroad, electrolytic cells capable of furnishing hydrogen at high pressure are obtainable, but are very costly.

Very promising methods for the production of hydrogen are: (1) The removal of carbon monoxide and

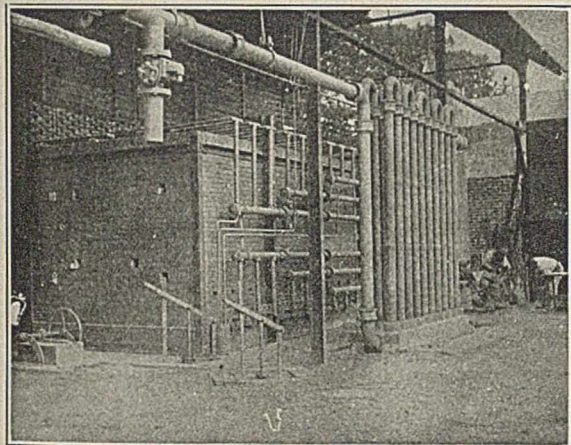


FIG. 27

hydrocarbons from water gas by liquefaction; (2) the decomposition of petroleum at high temperatures; and (3) the passage of water gas and steam at a temperature of 500°C . over lime containing an iron catalyst.

One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150 or 200°C ., hydrogen is surprisingly penetrating. A treating tank having an oil capacity of about one ton was tested to 150 pounds air pressure and found to be tight, but when hydrogen was introduced at 60 pounds pressure, the leakage was tremendous.

A stuffing box tested at 120 pounds steam pressure emulated a whistle, with hydrogen at *one-half* the steam pressure. Autoclaves with welded seams are desirable for high pressure and high temperature work. Moving parts should be avoided as far as possible.

USES OF HYDROGENATED OILS

The ability to prepare from ordinary *liquid* fatty oils a fatty body of almost any desired degree of consistency renders hydrogenation especially attractive in the production of edible fats and soap-making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have rather wide use in the arts. In the manufacture of lubricants, for example, the hydrogenated fats may be used to advantage.

HYDROGENATED OILS IN THE SOAP INDUSTRY

By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-

making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid having the formula $\text{C}_{18}\text{H}_{32}\text{O}_2$, which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap-making, this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap-making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

Crossfield & Sons¹ have patented, in some countries, the use of hydrogenated oil in the manufacture of soaps. They claim the hardened or hydrogenated fats have the advantage that a weaker brine suffices to separate the soap from the glycerine; further, that the soap produced from such hydrogenated fats is exceedingly hard; as, for instance, soap made from hydrogenated cottonseed oil is stated to be about 12 times as hard as that made from untreated cottonseed oil. This, of course, enables the admixture of a larger proportion of rosin, which naturally would be looked upon as a decided advantage.

In contrast to this, a German writer² states that the hardened oils form soaps which are too hard to give good lathering properties.

Since soaps are made almost invariably of mixtures of fats, it is under the control of soap-makers to use such an amount of hydrogenated fat as would give the requisite degree of hardness without sensible diminution in lathering power; hence the foregoing criticism seems to be without great weight.

It suffices to state that hydrogenated fats for soap-making purposes are being made abroad by a number of firms and are giving good satisfaction in many instances. The Germania works at Emmerich, Germany, offers on the market three grades of hardened oil.

In this country satisfactory results are being obtained commercially in the manufacture and use of hydrogenated oils in soap-making. Several plants are operating or planning to operate on the large scale.

EDIBLE HYDROGENATED OILS

Since the addition of less than 1 per cent. of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of the consistency of lard, it follows that manufacturers of ordinary lard compounds (that is to say, a mixture of 80 to 85 per cent. of refined cottonseed oil and 15 to 20 per cent. of oleo-stearine) have promptly turned their attention

¹ English Patent No. 13,042, of 1907.

² *Seifensieder Ztg.*, 39, 660.

to the production of the compound by a "self-thickened" cottonseed oil.

The high cost of oleo-stearine makes the method an attractive one and the hydrogenated product from cottonseed oil has the advantage, if properly made, of being very stable in character.

We believe, however, that for best results, it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take 20 per cent. or so of the oil and harden it to a titer of 52 or thereabouts and incorporate with unhydrogenated oil.

It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability.

EDIBILITY OF HYDROGENATED OILS

It seems to be generally accepted by those who have investigated the matter carefully that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived. It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature, hydrogenation renders the oil better adapted for human consumption.

A question of serious import has, however, arisen in the use of nickel catalyzer. Aside from the fact that by careless filtration, traces of the suspended nickel may be present in the product, there is the more serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed.

According to Bömer,¹ nickel is dissolved by oils during the hydrogenation treatment only when the oil contains free fatty acid in considerable amounts. A sample of hydrogenated sesame oil containing 2½ per cent. of fatty acid was found to contain 0.01 per cent. ash with 0.006 per cent. nickel oxide. Whale oil, containing 0.6 per cent. fatty acid, yielded 0.006 per cent. ash and 0.0045 per cent. nickel oxide. Such an amount of nickel presumably would not be tolerated in a product intended for edible purposes.

The Bureau of Animal Industry of the Department of Agriculture is now investigating the matter and apparently intends to determine the relative degree of toxicity of the traces of nickel in the form existing in improperly made hydrogenated oil. We may add that, so far as can be ascertained, the Department looks kindly upon the advent of hydrogenated oil in view of the likelihood that it is destined to prove a very acceptable substitute for higher priced animal fats and does not propose, according to my understanding, to venture any ruling until the matter has had protracted scrutiny.

It is our belief that the use of nickel in the form of an oxide, or the use of nickel catalyzer containing more than traces of oxide, is undesirable from the point of view of solubility in oil. Nickel, in the metallic state, cannot combine with a fatty acid to produce a soap, except with the elimination of hydrogen, and in the presence of an atmosphere wholly of hydrogen,

because of mass action, such reaction would not be likely to take place. On the other hand, nickel in the form of oxide would yield water on combining with fatty acid which would be yielded practically into a vacuum as regards the vapor pressure of water.

Hence it seems to the writer that in the manufacture of products intended for edible purposes, care should be taken to maintain conditions such that the catalyzer, if of the nickel type, is preserved almost wholly in the metallic state. Also it is desirable to not force the reaction too rapidly with the consequent danger of breaking down the carboxyl group and setting free water which would react to produce fatty acid.

Finally, it may be stated, by partial saturation of glycerides, we have the possibility of preparing from tri-olein the oleo-distearine or the dioleostearine. Dioleopalmitin would give either oleostearopalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearines, α - and β -oleo-distearine as well as α - and β -dioleostearine. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

MONTCLAIR, N. J.

BORON: ITS PROPERTIES AND PREPARATION¹

By E. WEINTRAUB

To the study of the chemical elements attaches a twofold interest. Their differences and similarities are a constant source of speculation, and any increase in the knowledge of their properties is an advance toward the discovery of the underlying laws of the constitution of matter. To the practical man the elements have the still further interest that they may have some unusual properties capable of technical application. All would like to learn the properties of such elements as uranium, titanium, and a number of others, and to know what they are good for.

The element boron is interesting from both points of view. It has exceptional characteristics—characteristics almost unique among elements, and it is also capable of practical uses of considerable importance.

In an article published in the 1909 Transactions of the American Electrochemical Society, Vol. 16, p. 165, the methods for the isolation of the element boron and the main properties of the element were described. The work has been going on steadily since then, mainly in the direction of developing the practical applications.

SPECIFIC RESISTANCE OF BORON

Among the characteristics of boron, the most interesting are those pertaining to its electrical resistance. The specific resistance of pure fused boron at ordinary temperature is very high, as compared to that of other elements which have any appreciable conductivity at all. Thus a piece of boron, regular in shape, two one-hundredths of a centimeter long and two one-hundredths of a centimeter square in cross section, has a resistance at 0° C. of nearly two and a half million ohms, or, in other words, 10¹² larger than

¹ Abstracted by W. R. Whitney from a lecture presented by Dr. Weintraub before the Eighth International Congress of Applied Chemistry, New York, September, 1912.

¹ Chem. Rev. Fett-Ilarz.-Ind., 1912, 221.

that of copper at ordinary temperatures. The element silicon, which comes next to boron, in resistivity, is still separated by a very considerable gap from it. The specific conductivity of boron at 0° is equal to about $0.5-0.6 \times 10^{-6}$ reciprocal ohms per cm./cm^{2.}, the conductivity of silicon is 1.8, or nearly a million times as large as that of boron.

NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE

This high specific resistance of boron is accompanied by a negative temperature coefficient of resistance, which is also unprecedented among elements. The resistance of boron drops very markedly as the temperature is increased, and it does this with exceptional rapidity at ordinary room temperature. At this temperature the conductivity of boron doubles in value for every seventeen degrees centigrade, as is illustrated by Fig. 1, where the temperature interval is 27°-450° C. The change in resistance is so great that it is difficult to represent the measurements on one curve, so two curves are used. In the first one the temperature interval is 27°-200° C. and the unit of resistance is a megohm; in the second one the tem-

sistance at 650° is too small to be represented even on the smaller scale of the last curve. At tempera-

Temperature Degrees Centigrade	Resistance Ohms
27	775,000
100	66,000
170	7,700
320	180
520	7
600	4

tures above 1000° the resistance is but a fractional part of an ohm.

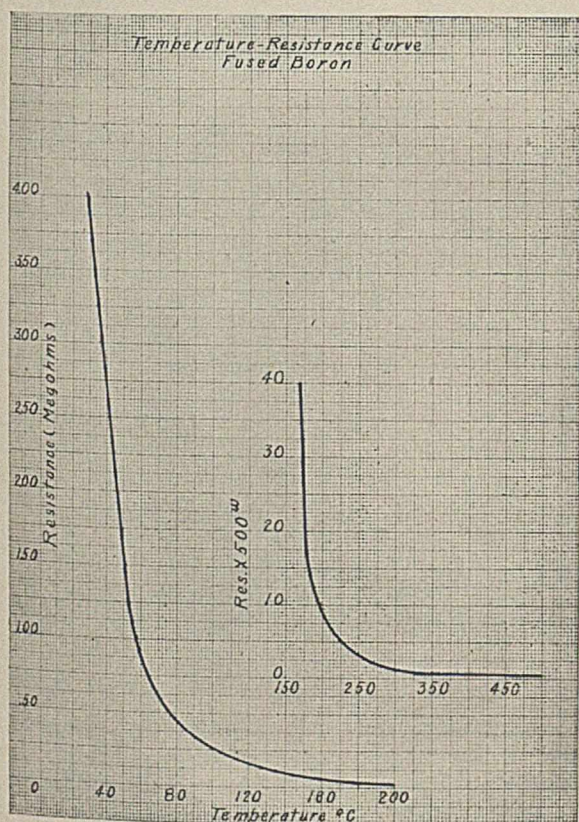


FIG. 1

perature interval is 200°-450° C., the unit of resistance is 500 ohms.

The following table gives measurements made on a very small piece of boron, which are plotted in Fig. 2.

Three ordinate scales are used, the resistance units being 10,000, 1,000 and 50 ohms, respectively, and the total temperature interval is room temperature to 650° C.

The cold resistance is 9,000,000 ohms and the re-

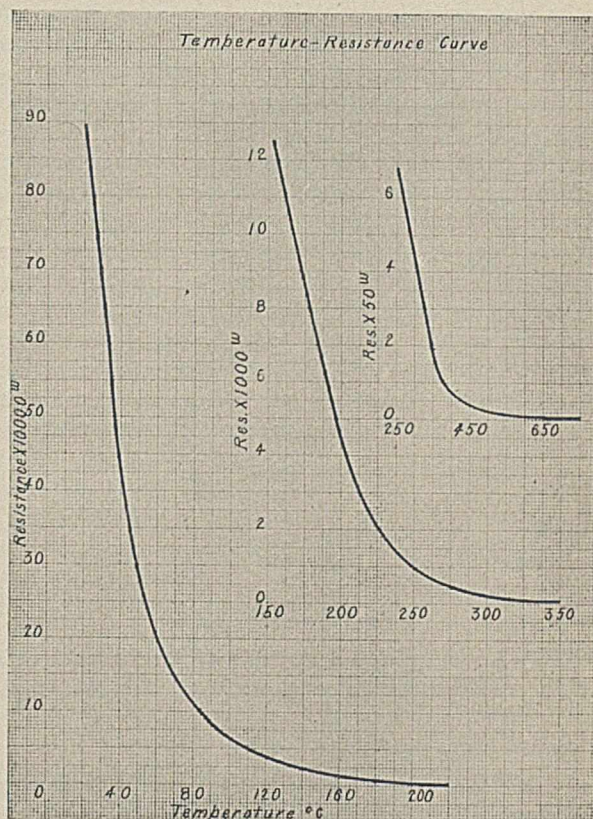


FIG. 2

The relation between temperature and resistance is not a simple one, but for small intervals of temperature it can be assumed that the drop in resistance is proportional to the resistance and the change in temperature, that is,

$$\Delta R = -\alpha R \Delta T.$$

At ordinary temperature the temperature interval, for which the resistance drops to half value is, as stated above, about 17°; this interval of temperature increases as the temperature rises, and at 600° it is about 80°. This leads to an exponential expression for the resistance which can be used for small intervals of temperature of about 50° with only a small error.

A comparison of this behavior of boron with that of other materials is instructive. It is generally known that metals have a positive temperature coefficient of resistance; in other words, their resistance increases with temperature. The metalloids have a negative temperature coefficient of resistance. Carbon, in its

amorphous form, has a slight negative temperature coefficient, its resistance dropping in the ratio of two to one between ordinary temperature and white heat. Silicon again comes nearest to boron, but the gap separating the two is again very considerable. Resistivity measurements on specimens of chemically pure silicon have never been made. It is, moreover, difficult to make consistent measurements on silicon on account of its tendency to crystallize in grains of different size and shape, but some specimens will show a drop of resistance as large as one hundred to one between ordinary temperature and the temperature near its melting point, which is about 1400°C .

Roughly speaking, therefore, between 0° and a good red heat the resistance ratio is for carbon, two to one, for silicon, one hundred to one, and for boron 10^6 or 10^7 to one.

Among compounds there are a large number with negative temperature coefficients of resistance. A familiar example is the Nernst Glower, which is a mixture of oxides and shows a very great drop in resistance with rise of temperature, which drop, however, begins, or at least becomes measurable only at high temperatures, 500° to 600°C . The same holds true for pure oxides. The drop of resistance of calcium oxide and of copper oxide from measurements made by Horton, are given in the following tables:

	Temperature	Resistance
Calcium oxide.....	763°	7×10^6
	1011	2×10^6
	1468	91
Copper oxide.....	12	462,400
	59	91,560
	134	12,360
	1038	0.02

While calcium oxide shows a drop of resistance only at high temperatures, copper oxide shows a rapid drop of resistance around room temperature, and in this way is very similar to boron.

The element boron then approaches in its electrical behavior more nearly certain compounds than the elements. As was pointed out in another place, it is the magnitude of resistance that determines the sign and value of the temperature coefficient of resistance and no fundamental difference exists in that respect between elements and composite substances.

Fig. 3 shows the relation between the resistance of boron and the watt input. This curve has not the theoretical importance of the temperature resistance curve, but is useful in connection with practical applications. The general course of the curve is the same as that of the temperature-resistance curve. The drop of resistance with watt input is so rapid that it is hard to represent it on one scale even with such a small variation of wattage as is embraced by the curve, namely, between 7 and 28 watts. The curve refers to a small piece of boron in air.

INFLUENCE OF DISSOLVED ELEMENTS

The influence of the addition of other elements dissolved in boron is no less interesting. This influence is of extraordinary magnitude, so that even as small an amount as 0.1 per cent. of carbon, for instance, will increase the conductivity of boron many fold.

When 7-8 per cent. of carbon are dissolved in boron the remarkable characteristics of boron disappear altogether and the material has a conductivity comparable to that of silicon or even carbon. The law of variation of the conductivity of carbon with the content of dissolved material is not established, but the experiments, as far as they have been carried out, point to an exponential curve. These experiments are as difficult as they would be interesting. One of the difficulties is the necessity of very accurate chemical analysis as a small error in the analysis would produce an enormous change in the curve.

It is again interesting to compare this behavior with that observed in other substances.

With metals the opposite case is true; if one metal is dissolved in another the resistivity increases, not

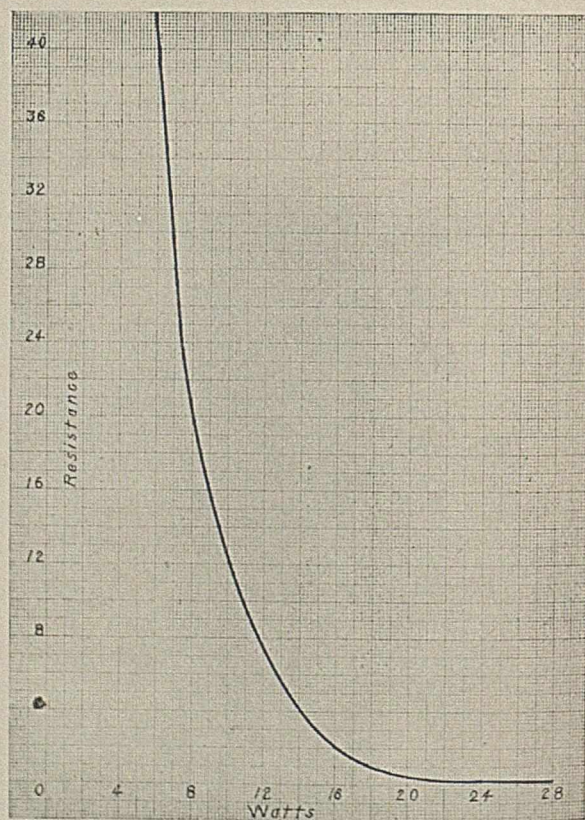


Fig. 3

the conductivity. Silver is a better conductor than copper, but addition of silver to copper increases the resistivity of the latter. With "poor" conductors, however, the conductivity of mixtures is greater than that of pure substances. This general behavior of poor conductors has been pointed out by the author previously.

Hand in hand with this diminution of resistivity goes the decrease in the value of the temperature coefficient of resistance. The temperature coefficient of resistance of solutions of elements in boron is still negative, but less so; so that while the difference in specific resistance at ordinary temperatures between boron and its solutions is very great, this difference becomes less and less as the temperature increases.

Finally, at high temperatures, in the neighborhood of 1000° there is very little difference in the conductivity of boron and the conductivity of dilute solutions of other elements in boron; all the resistance temperature curves seem to come together at high temperatures.

The reverse phenomenon has been observed with metals, but leading to the same final result. A solution of silver in copper is a poorer conductor than copper, but the temperature coefficient of resistance which is positive in this case is smaller than that of copper. At high temperatures the two curves will probably come very near together.

The rise in resistance, which takes place with good conductors, the drop in resistance which takes place in poor conductors, the above-described connection between the temperature coefficient and the magnitude of resistance all suggest the possibility that at a certain very high temperature all materials if preserved in solid or liquid form would show the same conductivity. What the value of that temperature is and what the theoretical significance of it may be are questions which will not be discussed here.

For the practical use of boron this influence of dissolved substances is very important, because one has it in his hand to change the specific resistance within very wide limits and also to change the temperature coefficient from the enormous value it has in boron to a very small value.

VOLT-AMPERE CURVE AND BREAKDOWN VOLTAGE

A consideration of the nature of the curve representing the relation of the *current and voltage* across a piece of boron is of importance. The volt-ampere curves of solids have not been used very much in theoretical discussion, for the reason that they have not the fundamental importance of the tempera-

according to conditions. These curves have, however, been used in the study of gaseous discharges to a great extent (Kaufman) for the simple reason that in this case the volt-ampere curve is the only thing that can be determined. In the study of the volt-ampere curve of solids or liquids three cases can be distinguished (see Fig. 4). If the resistance does not vary with the temperature, then the volt-ampere curve is a straight line and the tangent is a measure of the resistance (Curve I). For a material with a positive temperature coefficient of resistance (metals, etc.) the curve will be convex to the axis of abscissa (Curve II); in some cases when the temperature coefficient is large enough a part of the curve may run almost parallel to the axis of ordinates (Curve III). In other words, there may be a region in which a very large variation in volts corresponds to a very small variation in the current. This case is exemplified by iron, within a certain narrow interval, and also by tungsten. Placing these materials in hydrogen is favorable to this result, as the heat dissipation (conduction) at lower temperature is relatively more favored than at high temperatures (mostly radiation). For a material with a negative temperature coefficient the general form of the volt-ampere curve is represented by Curve IV. The resistance corresponding to 0 current is represented by the tangent of the angle and the whole curve will lie between this tangent and the axis of abscissae. This is because the volts rise more slowly than if the resistance remained constant. A few simple considerations will show that the curve will, in general, possess a *maximum*. From $E = RI$ it follows that

$$dE = RdI - I[dR].$$

$[dR]$ indicates the absolute value of the resistance change. For $I = 0$ one has, of course,

$$\frac{dE}{dI} = R.$$

For low values of current dE is represented essentially by RdI which is *positive*; therefore, the voltage first increases with the current. However, as the current increases the second factor, $I[dR]$ becomes more and more important; since the first factor containing R becomes smaller as the resistance drops, a point is finally reached where the two are equal. At this point $dE = 0$ and the voltage is a maximum. From this point on, $I[dR]$ will predominate and the volts will drop with increasing current. The general form of the curve is, therefore, that given by IV. It is seen that for the same value of voltage there correspond in general two values of current and that the curve consists essentially of two different parts, a rising part in which the conditions correspond to stability and a falling part which is essentially unstable. On this falling part no equilibrium is possible (unless there is external resistance in the circuit with a constant or rising characteristic). On constant voltage the current and the energy input (represented by the area of the curve) would increase until a condition equivalent to a short-circuit would take place. The point M which separates the two branches of the curve and which corresponds to the maximum voltage possible

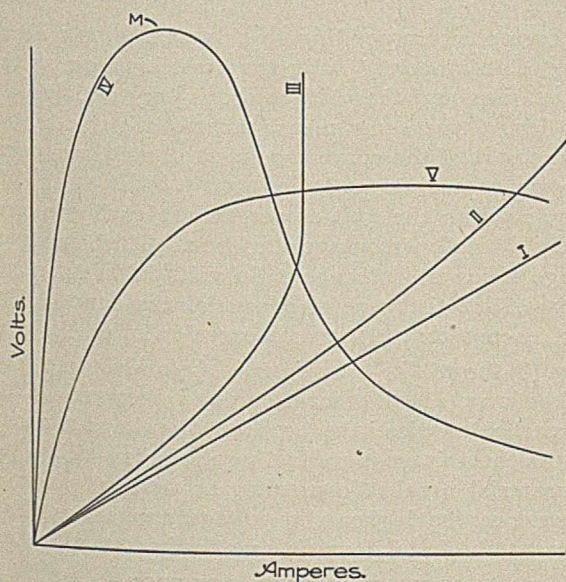


FIG. 4

ture resistance curve. The temperature resistance curve is perfectly definite; the volt-ampere curve will vary with the way in which the heat is dissipated. This is because a certain volt-ampere product means a certain watt input which may give any temperature

across the resistor will, on this account, be called the "breakdown" voltage.

It is at first sight somewhat difficult to see why the breakdown does not occur with ever so small a voltage since the energy introduced into the resistor should cause a drop in resistance; this in its turn causes an increased energy input, and so on. It will, therefore, be instructive to derive the existence of a breakdown point on the basis of energy relations. It will suffice to consider the very simple case in which constant voltage is applied, E . The energy input is equal to

$$W = \frac{E^2}{R},$$

and assuming that R is an exponential function of the temperature the energy input has the value

$$W = \frac{1}{C} E^2 e^{-\alpha T}$$

If the temperature at which the breakdown occurs is low (this is true of boron), one may assume that the dissipation of energy takes place only by heat conduction and therefore is proportional to the temperature difference and is equal to AT . At equilibrium, energy input and output must be equal. Hence, equation

$$\frac{E^2}{C} e^{-\alpha T} = AT.$$

By simple reasoning it is easy to see that this equality is possible only when E is below a certain critical value. When the volts exceed this critical value the equality is no longer possible at any temperature and the input will always be larger than the output. This particular voltage will correspond to the breakdown voltage. If the breakdown occurred at higher temperatures, the second part of the equation would contain a term corresponding to radiation, but the general conclusion would not be changed. Nor will it be materially affected if the resistance-temperature function is not exactly exponential.

The form of the curve discussed up to the present is characteristic of boron itself and all similar materials which have a very large negative coefficient of resistance. According to the value of this temperature coefficient and also to the values of the constants C and A (nature of the surface, of heat insulation) the curve may assume different forms. After the maximum voltage corresponding to M is reached the voltage may drop only very slightly or move along a horizontal part giving a constant voltage with varying current (Curve V) and finally the maximum voltage may lie at very high temperatures so that the falling part of the curve is not reached at all in ordinary work. In this case the curve is constantly rising, always remaining concave toward the X axis. The same form of volt-ampere curve may be obtained by combining a resistor with a positive temperature coefficient and one with a negative temperature coefficient of resistance, in series or in multiple.

These theoretical conclusions are illustrated by the following curves which are the result of actual measurements made on boron and on boron with a small percentage of carbon. Fig. 5 gives a volt-ampere curve obtained from measurements on a small piece

of pure boron in air. The contents were made by fusing on platinum wires. The first part, from 0 up to the maximum, rises very rapidly. The tangent of the angle this part forms with the axis of abscissa, gives the resistance of the material at room temperature. At 400 volts the breakdown voltage is reached.

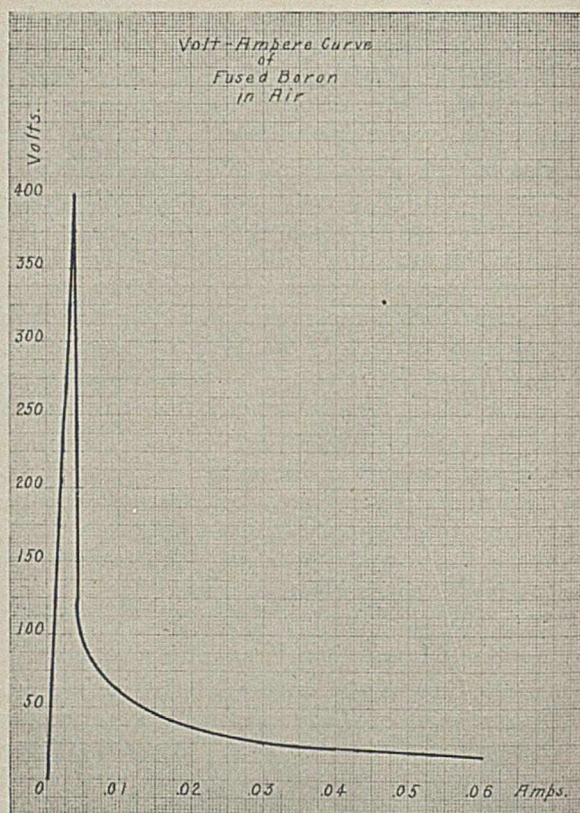


FIG. 5

The current corresponding to this part is only about 0.004 of an ampere. After the breakdown occurs the current rises and the voltage drops very rapidly.

In Fig. 6 the same measurements are represented but the part of the curve around the breakdown point is shown on a different scale.

Fig. 7 shows the volt-ampere curve of boron containing a small percentage of carbon. The breakdown voltage is lower, only about 80 volts in this particular case, but the general course of the curve is the same, except that the whole curve is lower.

Fig. 8 shows the *time interval* before the material breaks down at different impressed voltages. With this particular piece the breakdown voltage is about 85. As the voltage is gradually raised above this value the material breaks down after an interval which is the smaller the higher the voltage applied, until at 140 volts the breakdown is practically instantaneous.

OTHER PROPERTIES OF BORON

Boron is very hard. That would be expected, from the fact that boron carbide is a very hard material. Moreover, both boron and boron in which small percentages of other elements are dissolved can be prepared in a form in which they are tough to a certain extent, and in that way they differ from carborundum and

other artificial hard materials. The combination of these properties make possible their use for small bearings, such as meter jewels and for similar applica-

perfect polish. These methods have now been developed and meter jewels obtained, a large percentage of which are equal to diamond as to life and as to constancy of friction.

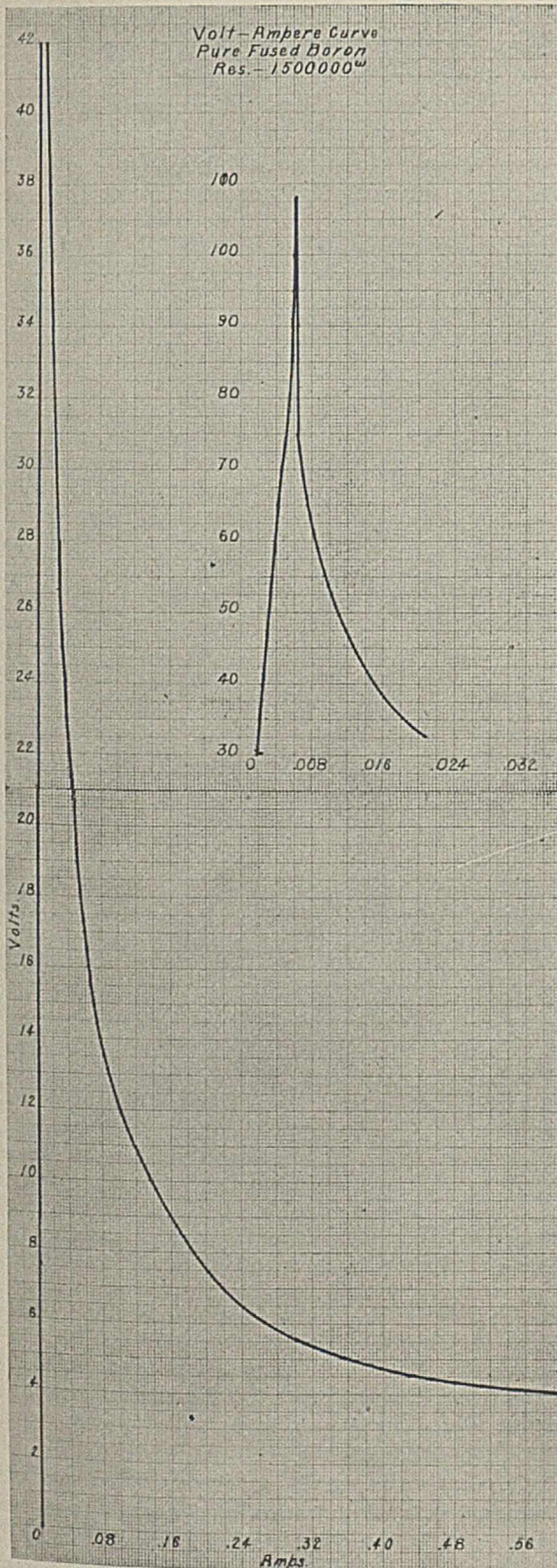


FIG. 6

tions. It has been, however, necessary to develop methods which would make a perfectly homogeneous material devoid of porosity and capable of taking a

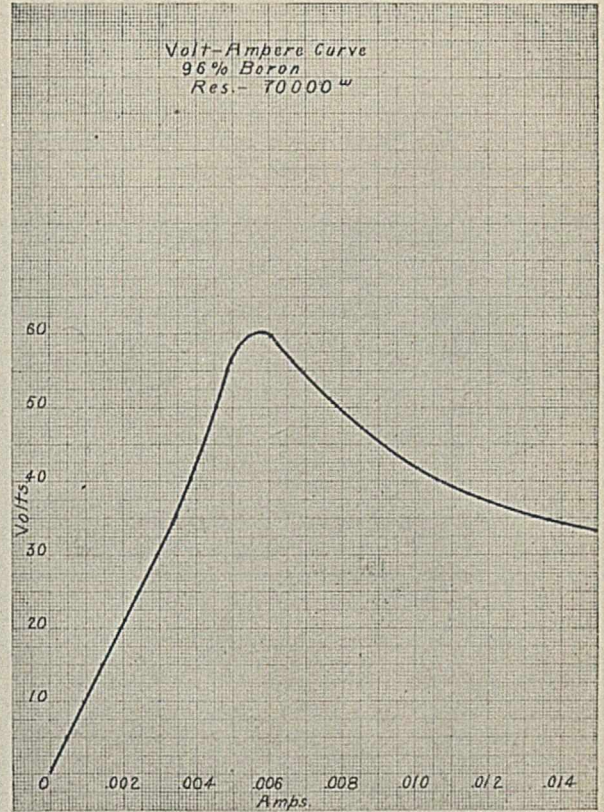


FIG. 7

CAST COPPER

Boron sub-oxide, a by-product obtained in the manufacture of boron, can be used for obtaining high conductivity cast copper. Copper cast without additions is full of pores and blow-holes, and therefore, mechanically unfit and of very low electric conductivity; the removal of the gases from copper by the known deoxid-

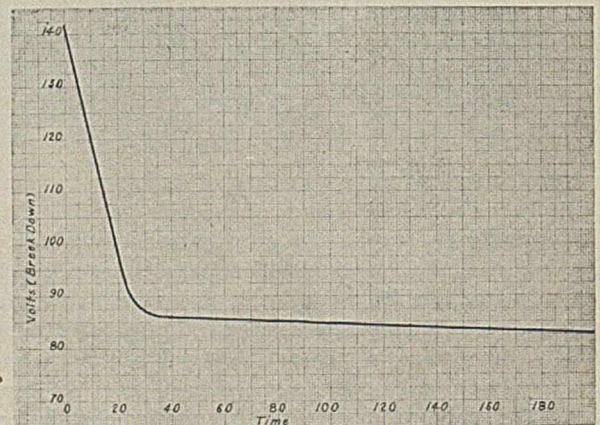


FIG. 8

izers is liable to give an alloy containing a small amount of deoxidizer, an amount sufficient, however, to lower the conductivity of the copper very consid-

erably. Boron sub-oxide, however, has the property of deoxidizing copper without combining with it, as boron sub-oxide has no affinity for copper. Tons of copper are cast now by this process, improving the quality of the product and at the same time cheapening it.

METHODS OF PREPARATION OF BORON

A brief description of the methods used to produce pure fused boron, also technically pure material in quantities, and to bring boron into definite shape, may be of interest. The methods are novel to a large ex-

Electrochemical Society, Vol. 16, p. 165 (Oct., 1909). This boron sub-oxide or magnesium boride compound is decomposed and the resulting boron melted in an arc. As boron sub-oxide is practically an insulator a high potential arc is used. Boron sub-oxide in a copper cup forms one electrode, the other is formed by a water-cooled copper electrode. The fusion takes place in an indifferent atmosphere, such as hydrogen. The arc is started with the two electrodes a certain distance apart by means of a high voltage, say 15,000 volts, delivering a relatively small current; when every-

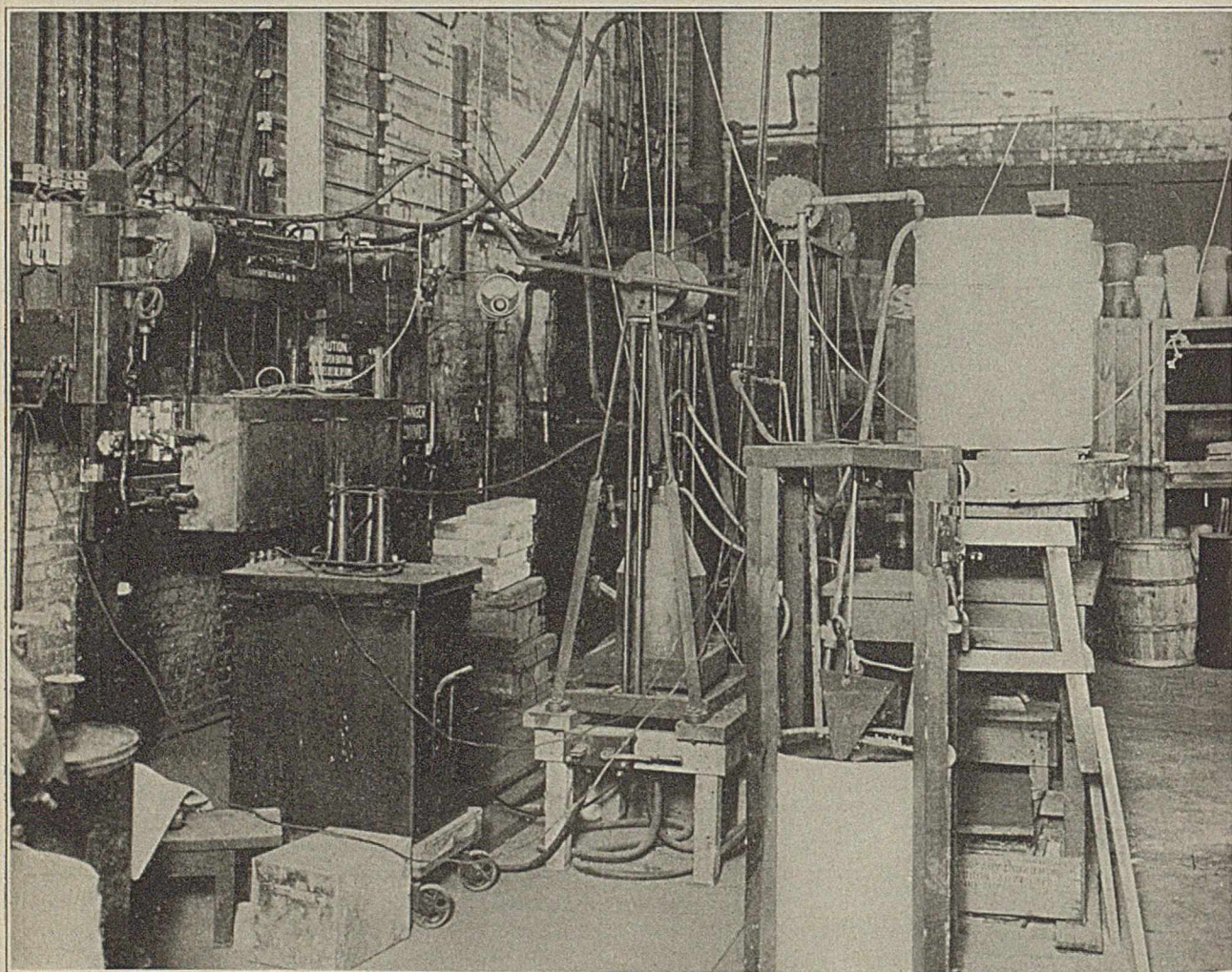


FIG. 9

tent and once developed in case of boron have shown themselves capable of applications in other fields.

The starting point in the preparation of technically pure boron is the reaction which has been studied before, the reaction between boric anhydride and magnesium or alkali metals. This reaction gives different products according to the relative weights of the substances employed, the temperature, and so forth. One interesting product obtained under certain conditions is boron sub-oxide of the approximate formula B_2O_3 . Under other conditions a product consisting of boron and magnesium boride is obtained. Detailed description of this reaction can be found in the article of 1909, in the *Transactions of the American*

thing is heated up the voltage is changed to about 2200 volts, the current to 50 amperes. After a while it is possible to reduce the voltage to 500 volts D. C. and increase the current to the desired value; by using 200-300 amperes it is possible to melt down a few pounds of boron at once.

Fig. 9 shows the small furnace used for some time but now replaced by a much bigger one. In this size of furnace only about a pound of boron can be melted in one operation. The iron hood can be moved up and down and through it hydrogen is flowing. Inside is a water-cooled copper cup containing the boron sub-oxide powder. Through the top a water-cooled copper terminal passes and is insulated from the hood.

A window is provided through which the operation of the furnace can be watched. The high voltage transformer and busbars conveying 2000 volts—(50 amperes and 500–700 volts—300 amperes, respectively)—are shown to the left of the furnace.

In this way it was found at first impossible to make absolutely pure boron. As long as the impurities are boiling out of the boron there is no danger of contamination with the material of the upper electrode; but when the state of purity of boron is approached the danger becomes considerable, and one has to stop a little short of absolute purity. With great care a material can be obtained containing about 99 per cent.

purposes they are apt to contaminate the material to be treated. They do not give a clear heat, that is, high temperature and nothing else. The new furnace is based on the use of a mercury electrode. It is a mercury arc furnace in an indifferent atmosphere.

Another method for making boron was developed before this one, and is capable of giving absolutely pure boron but is not as well adapted for producing large quantities. This method takes for its starting point boron chloride. If boron chloride is brought together with hydrogen at a high enough temperature it is reduced to boron and hydrochloric acid. All the materials taking part in the reaction are gaseous

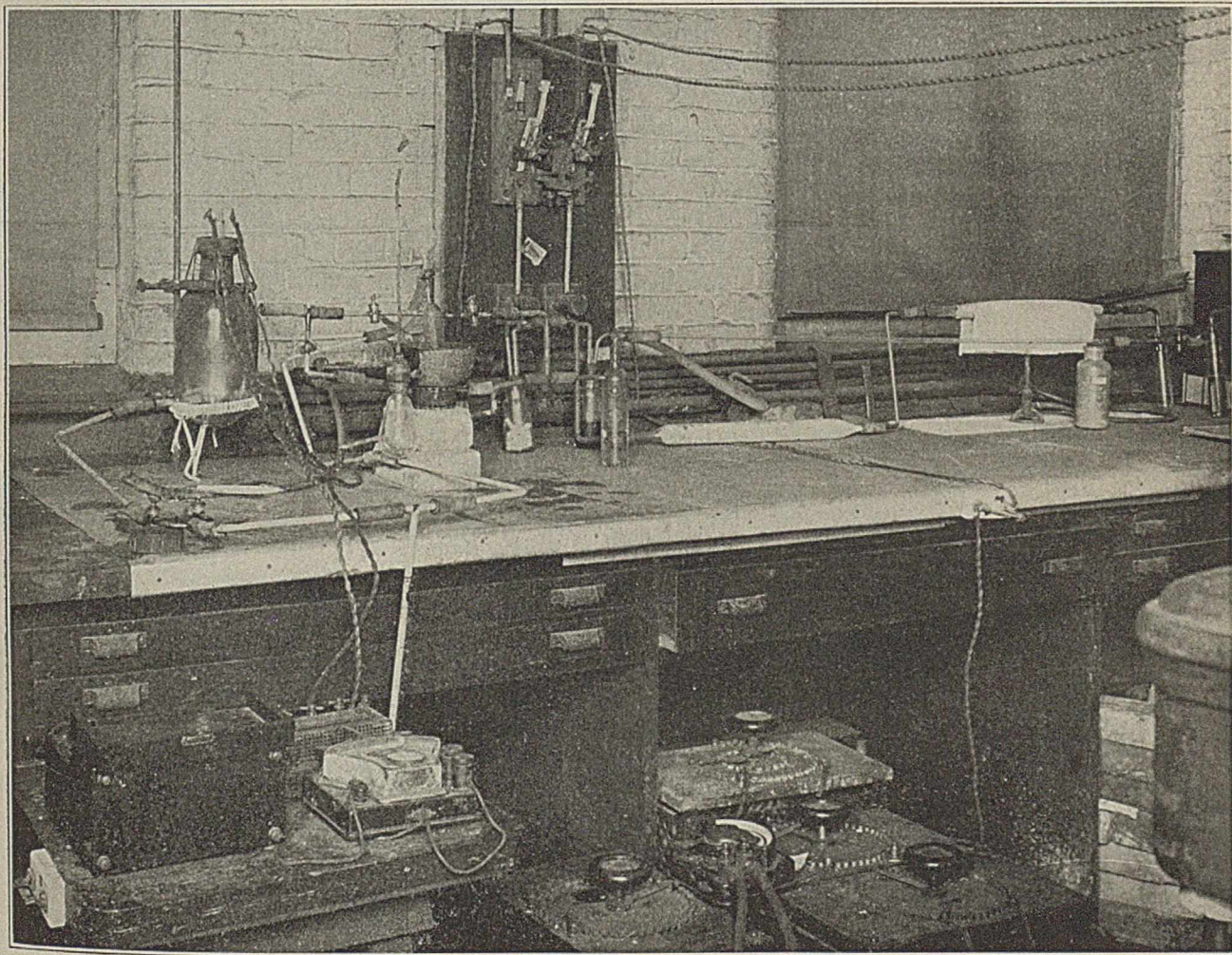


FIG. 10

boron. The average product will perhaps be not more than 97 to 98 per cent. boron. This product is good for some applications, but not for others.

It was necessary to develop an arc furnace in which no impurities at all would be introduced, either by chemical combination or mechanical admixture of the product of disintegration of the cooperating electrode. This has been accomplished and a furnace has been constructed in which practically any material can be melted down without introducing the slightest impurities into it. Most of the known arc furnaces use carbon electrodes or water-cooled metallic electrodes, and while they are excellent for some

except boron itself. As boron chloride can be made very pure and the slight impurities that may be in it are not reduced by hydrogen, the product is chemically pure boron in the most accurate sense of the word. If boron in the form of powder or lumps is wanted the reaction is carried out in an arc discharge between copper, or better, boron terminals. For practical applications (for making regulators, cut-outs, meter jewels) where a deposit of boron is wanted the gases are passed into a vessel in which a filament or plate is brought to incandescence by current.

The apparatus used is shown in Fig. 10. The hydrogen, freed from oxygen and dried in the usual way,

passes through liquid boron chloride which is kept at a definite temperature and the mixture passes then through the vessel on the left, where it is caused to react by the incandescent body. The procedure is modified in case it is desired to deposit a definite amount of boron. A vessel of definite dimensions is then filled with boron chloride and hydrogen of definite pressure.

SHAPING BORON

The arc furnace delivers irregular lumps of boron. Starting with these, the problem is to make a rod of boron. Casting in a mold is excluded because the

material is to be used for the envelope? The temperature must be high around 2300° . At that temperature the material must not have an appreciable conductivity or else it would take current itself, but above all it must not attack boron. Boron is very active at high temperatures and attacks practically everything known, all oxides included. The solution of the difficulty was found in the use of a boron compound—boron nitride, a substance described in all books of chemistry, but whose physical properties have not been well known. It is infusible, even at the temperature at which tungsten melts. More than

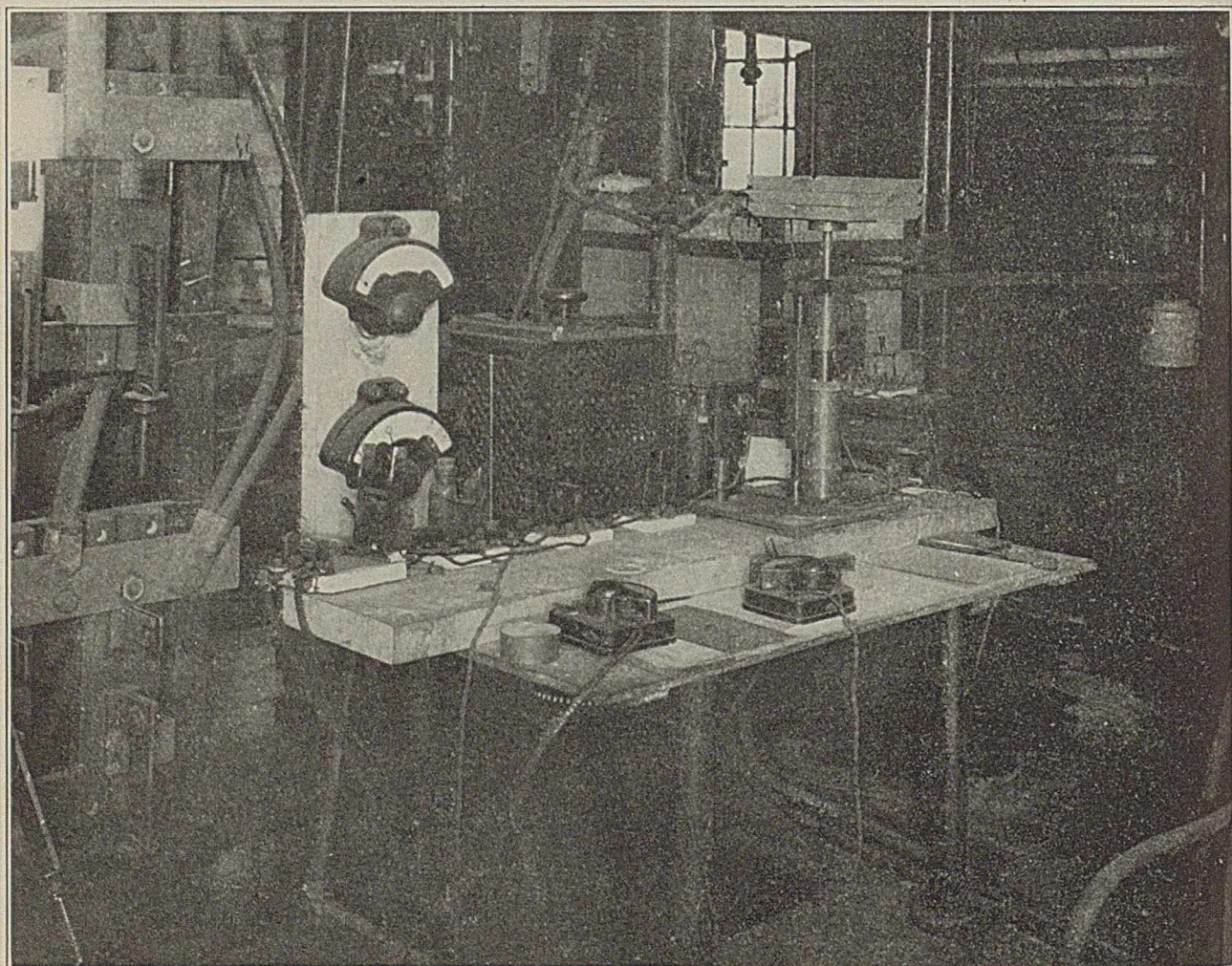


FIG. 11

melting point of boron is about 2300° C. It was found impossible to agglomerate the very hard boron by mere compression. The use of binding material would introduce impurities; but even if the material were agglomerated, the subsequent sintering by current would be a difficult matter on account of the large negative temperature coefficient resistance of boron. The current has a tendency to concentrate in lines which happen to have a higher conductivity; streaks develop, causing melting through in points before the whole mass is sintered. It was necessary to surround the boron with an envelope which would equalize the temperature and preserve the shape. But what ma-

terial, boron nitride is a very poor electrical conductor at high temperatures, much poorer than any other known insulator. For instance, a small disc of magnesium oxide $\frac{1}{8}$ inch thick passed in some of the tests an appreciable current at 800° C. with 110 volts applied. A disc of boron nitride of the same dimensions heated at 1200° C. and put across 500 volts gave no measurable current. These two properties, infusibility and high insulating power at high temperatures, make it the ideal substance for an envelope in sintering boron. One more thing is necessary in order to make the sintering furnace complete; it is necessary to insure good contact between

the boron powder and the electrodes which conduct the current to it. This was done by applying pressure, and so a new type of furnace was developed, the "boron nitride sintering furnace." With this furnace not only boron, but also boron carbide, tungsten, and a large number of other materials have been formed into rods. On account of the inertness of boron nitride almost any refractory material can be sintered in this furnace, and it is difficult at present to foresee all the possibilities of this furnace in the direction of sintering materials or combining materials at elevated temperatures under high pressure.

Of course, in order to use boron nitride in this furnace, methods had to be developed for making boron nitride relatively cheaply and in large quantities. Fig. 11 shows a small size boron nitride furnace.

Due credit is given to the men of the West Lynn Research laboratory of the General Electric Co. who ably assisted in this work—G. Wejntraub (work on the arc furnace, on the boron nitride furnace, etc.), H. Rush (designing of boron nitride furnace), E. Kraus (boron chloride reaction), F. W. Lyle (development of applications of boron to electrical engineering) and F. Kroner (copper casting). To them the success of this investigation is largely due.

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ACETYLENE SOLVENTS¹

By JOSEPH H. JAMES

The rapidly advancing price of acetone makes it desirable to have commercially available a solvent that can be obtained in any quantity and which shall not advance in price abnormally.

To determine the relative industrial value of various acetylene solvents, a number of laboratory tests and large scale experiments were made. The purpose of this paper is to report the results of this work.

The acetylene used in the laboratory tests was made from commercial carbide in an ordinary "Carbide to water" laboratory generator. It was purified to remove ammonia, sulfur compounds, and phosphorus compounds, by passing through a purifying train consisting of the following: (1) a ten per cent. sulphuric acid solution, (2) a fifteen per cent. hydrochloric acid solution saturated with mercuric chloride, (3) two towers, each containing approximately equal parts of a mixture of bleaching powder and slaked lime, (4) slaked lime, (5) two towers of fused calcium chloride.

In order to get as closely as possible at the true figure for the absorption of acetylene in any of its solvents, it is necessary that the gas be free from impurities and that the solvents be of the highest purity attainable. It has been demonstrated that the solubility drops off rapidly when impurities are present, either in gas or solvent. To get the highest commercial efficiency it will pay to purify the gas and select solvents of highest purity. Care with reference

to the purity of gas and solvent is at present not given the attention in this industry that it deserves.

The detailed method of carrying out this absorption test was as follows:

A carefully measured volume of the solvent (usually 1.5 cc.) was placed in an ordinary five inch side neck test tube, fitted through a two-hole rubber stopper with a glass tube gas inlet, and a thermometer, the bulb of which was immersed in the solvent.

This tube with solvent was immersed in a freezing mixture (ice and salt) and cooled to -18° or -19° C. before starting. The purified gas circulated through a four foot coil immersed in the freezing mixture, thus bringing the gas to the temperature of the solvent.

The acetylene was bubbled through the absorption tube at the rate of about one bubble per second. Since volatile solvents are appreciably vaporized during this process of saturation, the exit gas and vapor in each case was passed through an ordinary potash bulb containing 95 per cent. alcohol; thus the amount of vaporized solvent was determined and proper correction made on the volume of solvent actually used. In twelve minutes the amount of solvent usually taken was completely saturated with the gas at atmospheric pressure; pressure and temperature were always noted. The exit of the absorption tube was then connected to a similar tube two-thirds full of saturated calcium chloride solution which in turn had been saturated with acetylene. The calcium chloride was connected to an ordinary Hempel measuring burette (the liquid in the latter also being a saturated solution of calcium chloride subsequently saturated with acetylene).

The purpose of the calcium chloride was to absorb any solvent vapor that might be carried out in the evolution of the gas, and which would otherwise be measured with the gas giving too high a result. The saturated calcium chloride solution has a very low absorptive capacity for acetylene and it has been proved that it condenses and absorbs completely the vapors of each of the solvents tested. The efficiency of the saturated calcium chloride as an absorbent for the vapor of the various organic liquids used for acetylene solvents was demonstrated by boiling the solvents, and passing the vapor into such an absorbent tube, when the absorption was found to be complete. In several of the experiments noted below, evolved gas from the measuring burette was bubbled back through a "potash" bulb containing 95 per cent. alcohol, but no trace of solvent was found.

Gas evolution begins soon after the absorption tube is removed from the freezing mixture. While the solvent was saturated at -18° C. usually, to guard against the possibility of the solvent not being saturated at the place taken as the starting point, the readings were not noted until the temperature of the solvent had risen to -10° C. The gas evolved from a known volume of the solvent, saturated at -10° C. (since if gas is evolved between -18° and -10° it must be saturated at -10° C.) up to 30° C. is then measured, the figure obtained being recorded in each of the de-

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

terminations noted below. The readings are given as actually obtained under the pressure and temperature conditions of the laboratory, and this gas volume is reduced to 0° C. and 760 mm. pressure.

The reason for selecting -10° C. as a point at which the absorptions were determined, was that in commercial practice it is very easy to cool the containers to this temperature. The 30° C. figure was obtained

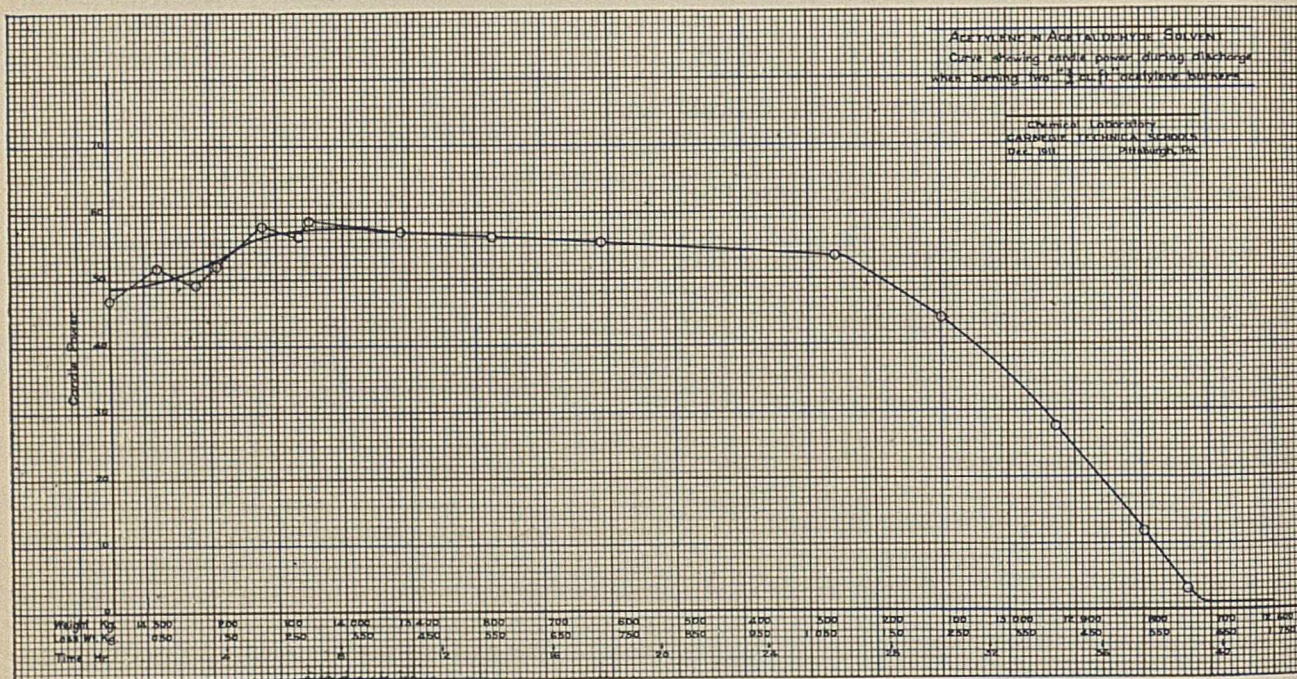


FIG. I—ACETYLENE IN ACETALDEHYDE SOLVENT
Candle power during discharge when burning two $\frac{3}{4}$ cu. ft. acetylene burners

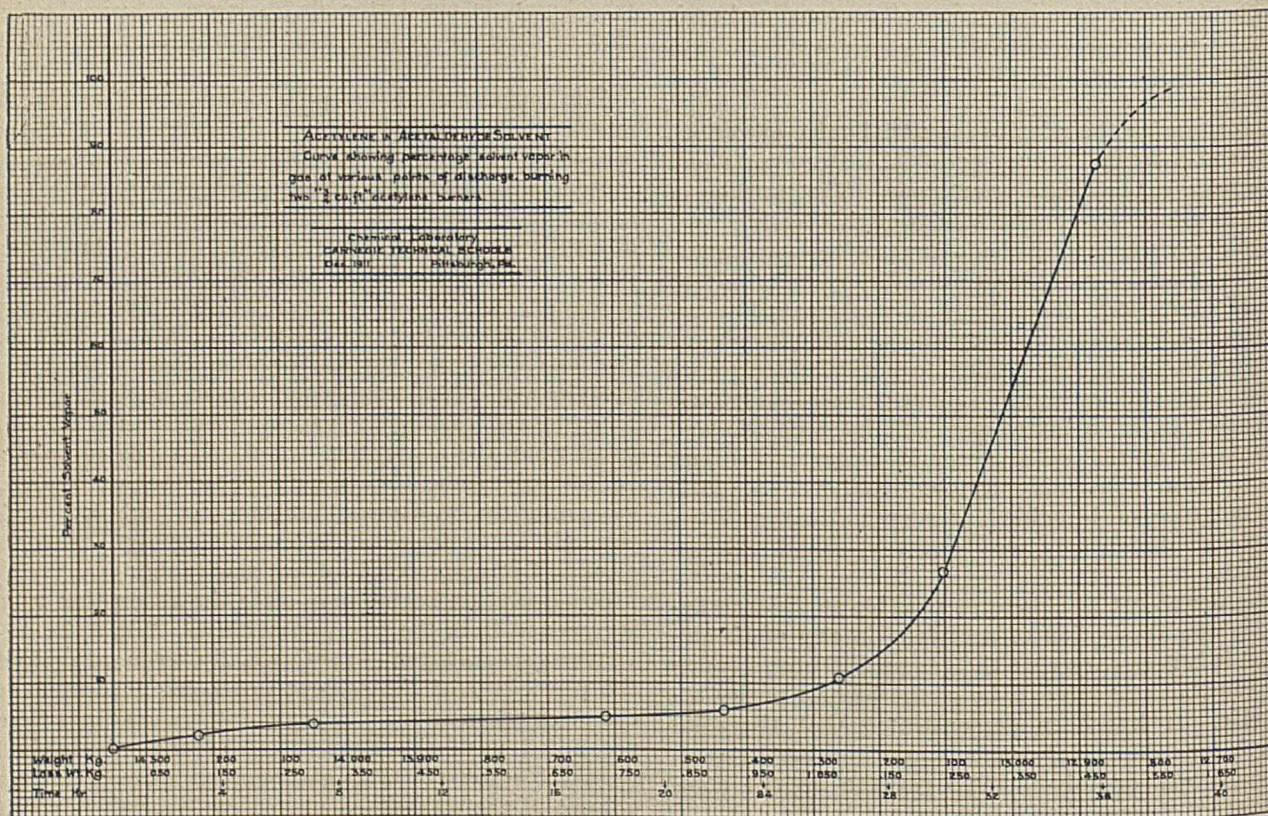


FIG. II—ACETYLENE IN ACETALDEHYDE SOLVENT
Percentage solvent vapor in gas at various points of discharge, burning two $\frac{3}{4}$ cu. ft. acetylene burners

for the reason that with this data the behavior of the solvent could be predicted in practical use, where the gas is rarely evolved at a temperature above 30° C.

absorption value of acetone far exceeded that of any solvent studied previously, and some preliminary skirmishing among organic liquids soon led to the view

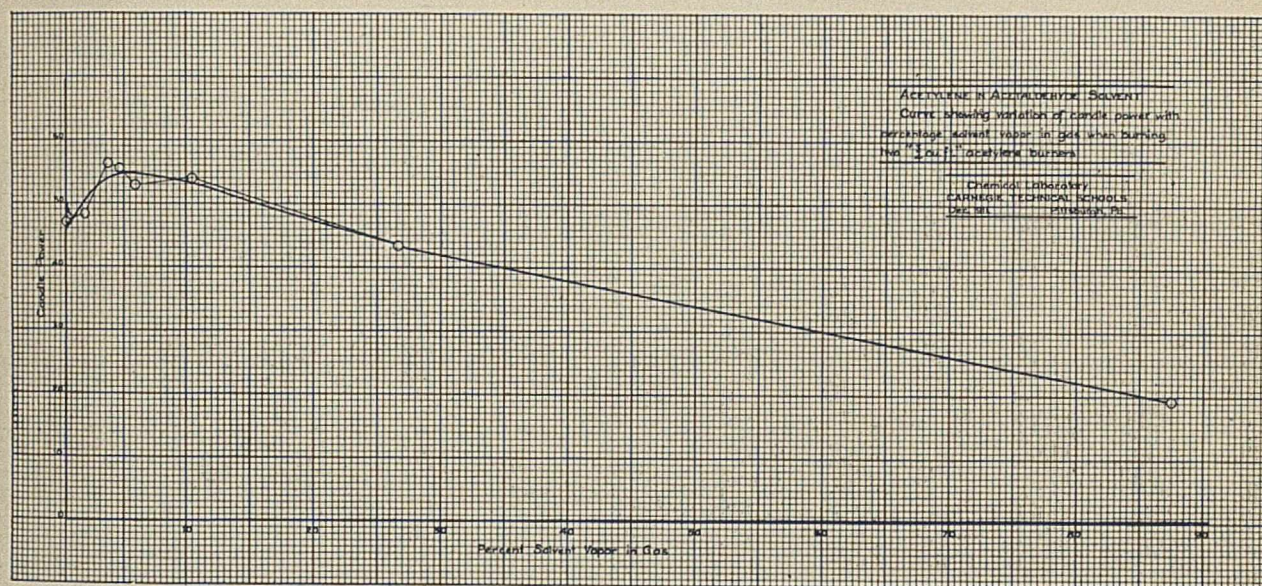


FIG. III—ACETYLENE IN ACETALDEHYDE SOLVENT
Variation of candle power with percentage solvent vapor in gas when burning two $\frac{3}{4}$ cu. ft. acetylene burners

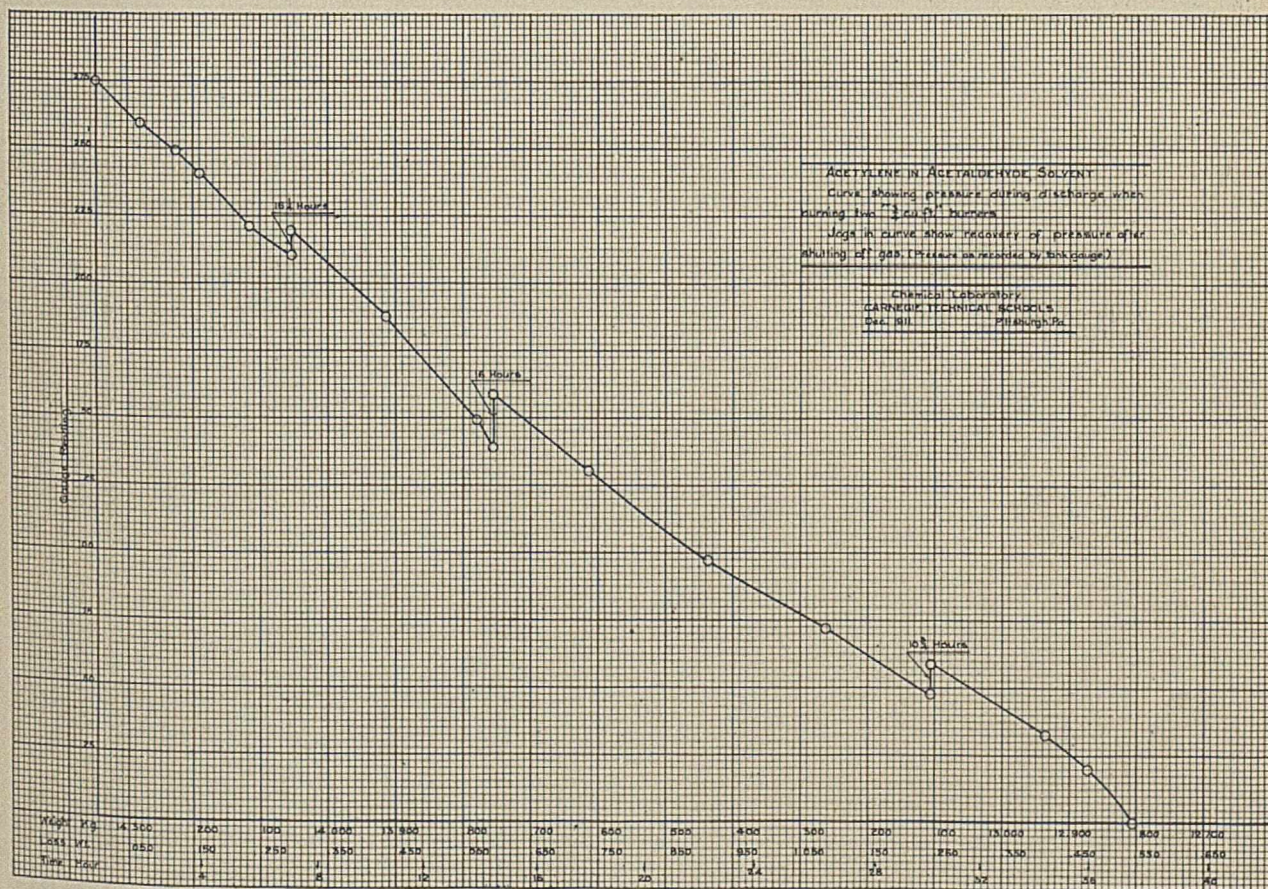


FIG. IV—ACETYLENE IN ACETALDEHYDE SOLVENT
Pressure recorded by tank gauge during discharge, burning two $\frac{3}{4}$ cu. ft. burners. Jags in curve show recovery of pressure after shutting off gas

LABORATORY RESULTS

The work of Claude and Hess¹ had shown that the

that the absorption of acetylene in acetone and other carbonyl compounds is partly chemical, in the sense that a chemical reaction or a partial reaction takes

¹ *Compt. rend.*, 124, 626.

place between the molecules of the absorbent or solvent and molecules of the acetylene. It is well known to organic chemists that the carbonyl group is a very

activity here is quoted in support of von Baeyer's "Strain Theory."

With the conception then, that the carbonyl group

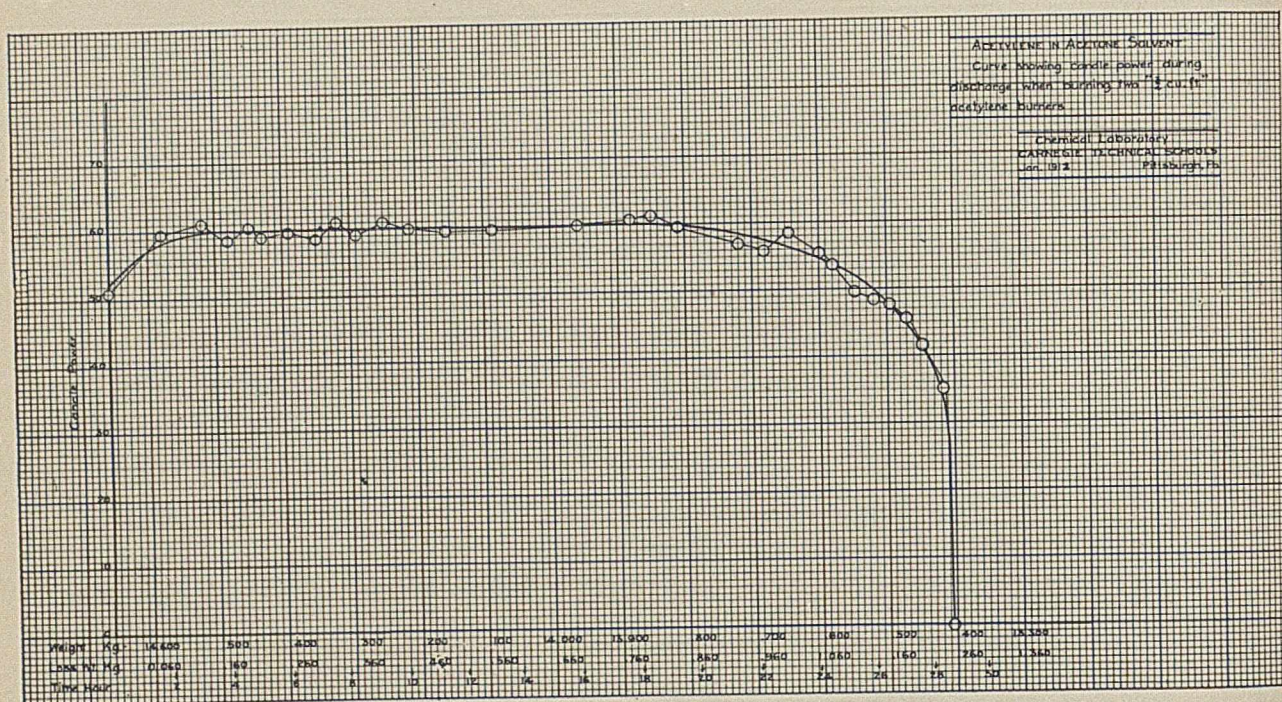


FIG. V—ACETYLENE IN ACETONE SOLVENT
Candle power during discharge when burning two $\frac{3}{4}$ cu. ft. acetylene burners

reactive point in the molecule of many carbon compounds, in fact this indicates a condition of strain between the carbon and the oxygen, and the ready

in acetone is the reactive point, and that a chemical action of some kind takes place, the solvents noted below were tested. The results establish pretty clearly

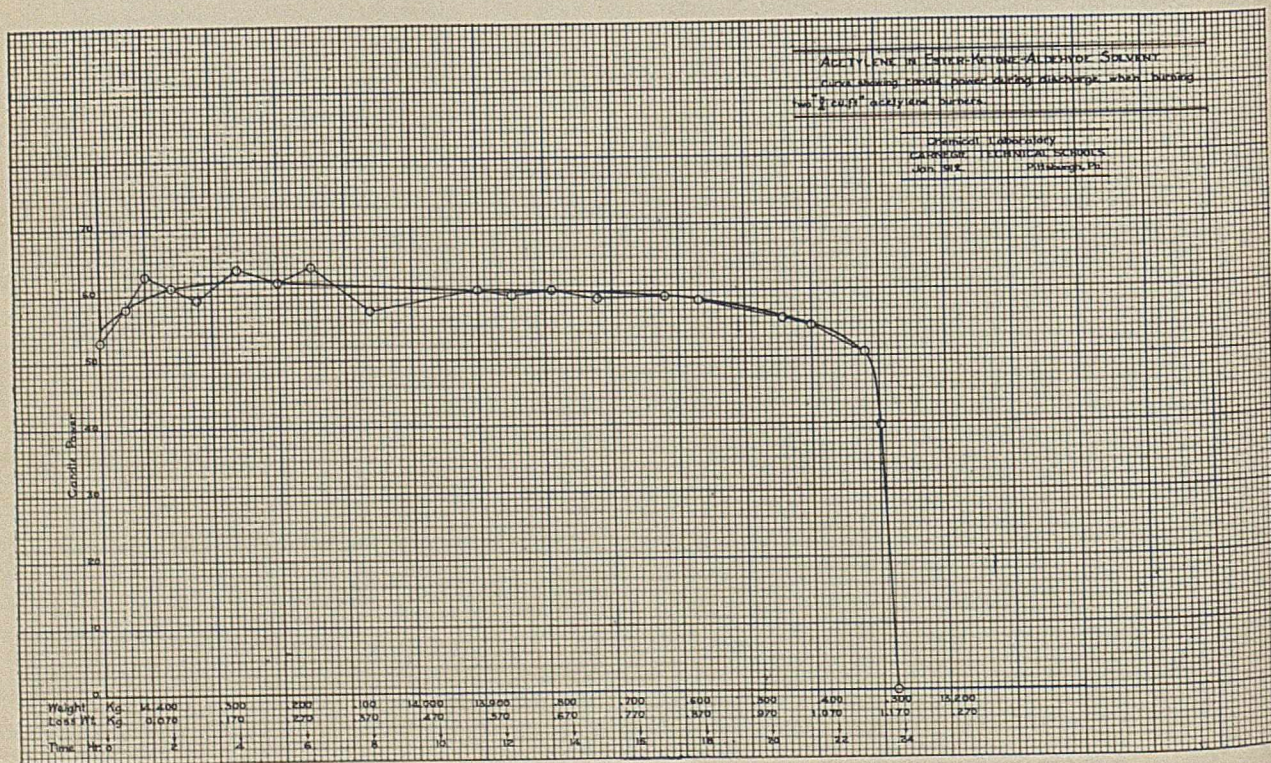


FIG. VI—ACETYLENE IN ESTER-KETONE-ALDEHYDE SOLVENT
Candle power during discharge, burning two $\frac{3}{4}$ cu. ft. acetylene burners

that there is a close relation here between the structure and the absorption capacity of a given com-

TABLE I—SOLUBILITY OF ACETYLENE AS DETERMINED BY PREVIOUS OBSERVERS

Solvent	Temperature, Degrees C.	Acetylene dissolved by 1 vol. solvent	Observer
Acetone.....	15	25	Claude & Hess
Acetic acid.....	18	6	Berthelot
Alcohol.....	18	6	Berthelot
Benzoline (gasoline).....	18	4	Berthelot
Chloroform.....	18	4	Berthelot
Paraffin oil.....	0	1	E. Miller
Paraffin oil.....	18	1.5	Berthelot
Carbon bisulphide.....	18	1	Berthelot
Olive oil.....	..	0.48	Fuchs & Schiff
Carbon tetrachloride.....	0	0.25	Nieuwland

TABLE II—PRELIMINARY WORK ON SOLUBILITY OF ACETYLENE
(Figures refer to volume absorbed at -10°C ., but volumes are not reduced to standard conditions)

Name	Solvent Boiling point $^{\circ}\text{C}$.	Acetylene dissolved by one vol. solvent at -10°C .	Remarks
Ethyl mustard oil.....	131.5	3.2	
Ethylidene cyanhydrin....	183.0	2.8	
Acetoacetone.....	137 $^{\circ}$	10.2	
Benzophenone, 1 gram dissolved in 23 cc. acetophenone.....			Saturated at 12 $^{\circ}\text{C}$., 1.7 volumes absorbed
Methyl propyl ketone.....	102.0	14.8	A crystalline compound of acetylene and acrolein forms during absorption.
Butyric aldehyde.....	74	10.3	
Acrolein.....	52	22.6	
Propionaldehyde.....	48.9	24.2	
Acetaldehyde.....	21	54	
Acetaldehyde, 50 per cent by volume	36	42.2	
Acetone, 50 per cent. by volume			
Acetaldehyde, 50 per cent. by volume	43	40.2	
Ethyl acetate, 50 per cent. by vol.			
Acetaldehyde, 50 per cent. by vol.	32	31.1	
Propionaldehyde, 50 per cent. by vol.			

"Carbonyl theory" is not a complete enough one.

There is also a relation in a given series, usually, between the molecular weight and the absorptive capacity.

The figures obtained are arranged in the preceding tables, the values determined for acetone and certain other organic liquids by previous observers being given for comparison.

SUMMARY OF LABORATORY RESULTS

A study of the figures obtained establishes pretty conclusively that of all the liquids tried, those organic compounds containing the carbonyl group are the best solvents for acetylene. We must exclude the organic acids, as the presence of the free hydroxyl hydrogen seems to work counter to the chemical action upon which the remarkable solubility seems to depend. That the "carbonyl theory" is not satisfactory in every respect is shown by the high figures obtained for methylal and acetal. Their peculiar action seems to require the assumption of quadrivalent oxygen for an adequate explanation.

Further, the figures clearly establish that in a given series the absorption of acetylene is greater the lower the molecular weight of the compound. The above experiments had in view the selection of a solvent that could be used industrially. Since the esters and acetals are out of the question industrially, requiring two and three molecular units per molecule of product, respectively, it was decided to try some larger scale experiments with acetaldehyde, making comparisons with other solvents in commercial use. The amount of acetylene absorbed increases under pressure approximately according to Henry's Law, so the above laboratory results can be used to predict pretty closely what will be absorbed under the pressure used in the acetylene storage industry.

LARGE SCALE EXPERIMENTS

In this series acetaldehyde of between 99 and 99.5

TABLE III—ABSORPTION FIGURES ON ACETYLENE SOLVENTS

SOLVENT	Boiling point $^{\circ}\text{C}$.	CC. ACETYLENE EVOLVED				Laboratory temperature $^{\circ}\text{C}$.	CORRECTED VOLUME ACETYLENE EVOLVED		AVERAGE ¹ ABSORPTION
		Per cc. solvent		Per cc. of solvent			Barometer reading, mm.	Per cc. of solvent at -10°C .	
		-10°C . to 30°C .	-10°C . to b. pt. of solvent	-10°C . to 30°C .	-10°C . to b. pt. of solvent				
Acetaldehyde, C. P.....	20.8	0.76	50.4	66.3	23.0	745	59.9	60.2	
		0.81	52.6	65.0	22.0	745	58.8		
		1.44	98.8	68.6	21.5	742	62.1		
Methylal, C. P.....	45.5	1.0	45.2	60.3	25.8	735	39.9	54.3	
		1.0	45.4	62.4	25.4	735	40.1		55.2
Acetal, C. P.....		1.0	20.4	30.7	18.8	742	18.7	28.8	
Methyl formate, C. P.....	32.3	1.5	70.8	81.5	25.6	742	42.1	48.5	
		1.5	69.4	80.9	23.5	738	41.4		48.2
Ethyl formate, C. P.....	54.5	1.5	46.1	71.1	24.5	738	27.4	42.2	
		1.5	46.0	70.8	24.4	738	27.4		42.0
Isoamyl formate, C. P.....	123.0	1.5	15.6	30.0	23.2	739	9.3	17.5	
		1.5	15.9	28.7	23.8	739	9.5		17.1
Methyl acetate, C. P.....	57.5	1.5	61.3	82.8	22.2	735	36.6	52.3	
		1.5	61.1	91.5	21.4	738	36.6		55.0
Ethyl acetate, C. P.....	77.0	1.5	48.9	72.6	18.4	742	29.9	44.5	
		1.5	48.4	71.8	17.2	742	29.6		44.6
Isoamyl acetate, C. P.....	139.0	1.5	28.8	46.0	23.4	739	17.2	29.3	
		1.5	29.0	51.7	21.8	738	17.4		31.0

¹ Average from preceding column.

ound for acetylene, although the figures obtained for methylal and acetal would indicate that the

per cent. purity was used as the solvent in a regular 6 X 20 inch acetylene storage tank, such as is commonly

used on automobiles, in order to make comparisons with solvents in industrial use as to the amount of gas absorbed, the candle power of the light given on burning the gas from the tank, the loss of solvent, etc. The other solvents were c. p. acetone and a complex mixture of organic liquids, which is used as a solvent for acetylene, and which will be referred to in the accompanying curves as ester-ketone-aldehyde solvent since it undoubtedly owes its absorbent power to the presence of bodies belonging to these three groups.

Probably the most important point of comparison is brought out in the curve for each solvent where the candle power at various times of the discharge is shown; a striking difference between the volatile and the non-volatile solvents appears here. With the non-volatile solvents there is little more than an hour's warning before the gas is gone completely, while with the volatile acetaldehyde solvent there is an interval of from four to six hours in length from the first warning and the "going out" of the light. With the acetaldehyde, there is a round black spot in the flame that makes its appearance at about the 35 candle power point of the curve, and the size of this spot increases as the candle power drops, its appearance giving about six hours warning, where two $\frac{1}{2}$ cu. ft. burners are being used.

The loss of solvent, which runs in common practice with the nonvolatile solvents from 4 to 6 ounces for each discharge of the tank, was a fraction over 12 ounces in the acetaldehyde experiment, where the evolution of the gas was pushed to the limit, and would undoubtedly run about 8 ounces in industrial use.

At first glance it appears rather surprising that the drop in candle power with the increase of solvent vapor in the gas is not greater. For example, it is seen from the curve where candle power is plotted against per cent. of solvent vapor in the gas, that when the solvent vapor has increased to 80 per cent. the candle power is still above 20. It has been noted by other observers that diluents lower the candle power of acetylene more rapidly, the lower the flame temperature of the diluent. Since acetylene has a heat of 313.8 cal. per gram molecule, and acetaldehyde has 279.2, we have a satisfactory explanation of the action of the diluent in this case; the calculated temperature of the hottest part of the oxy-acetylene flame is in the neighborhood of 4000° C. and that of the oxy-acetaldehyde flame is above 3400° C.

The aldehyde vapor is a good diluent also for the reason that the volume of air or of oxygen required for its combustion is theoretically exactly the same as that required for acetylene, so that there is scarcely any change in the shape of the flame, as the percentage of aldehyde vapor increases.

These two facts, the high heat of combustion and the equality of the volume of air or of oxygen needed, make for an advantage in the use of acetaldehyde as a solvent for acetylene to be used in welding and cutting operations. In an emergency repair job in a remote locality, in case the gas gives out, the work can be finished by drawing on the volatile solvent for the combustible.

Long observation has shown that the figures attained in industrial practice with the non-volatile solvents noted above, average 37 ounces acetylene in 85 ounces solvent, at a temperature of 70° F. and a pressure of 250 pounds gauge. In this experiment with acetaldehyde as the solvent, 48 ounces of acetylene were absorbed in 82 ounces of solvent, with the gauge standing at 265 when the temperature rose to 70° F. This figure shows that acetaldehyde is a liquid that has a superior absorbent power for acetylene; in fact, the author ventures the statement that this experiment shows an amount of acetylene greater than has ever before been stored in a given volume of solvent.

CONCLUSIONS

I. Acetaldehyde fulfils the industrial requirements for an acetylene solvent.

II. The volatility of acetaldehyde can actually be turned to advantage.

III. Since acetaldehyde can be made in one chemical operation directly from denatured alcohol, we have here a source of supply of an acetylene solvent which will not increase in price, but which will undoubtedly become cheaper as improved methods of agriculture make it possible to produce denatured alcohol cheaper.

Acknowledgment.—I am indebted to my former student assistants, Messrs. E. P. Poste and E. W. Gardner, for their help in taking readings and making records in the above experiments. I wish also to express my thanks to Dr. H. S. Hower, of the Physics Department, Carnegie Institute of Technology, for assistance in taking the candle power readings and for the loan and standardization of the Brodhun Portable Photometer, which was used in the photometric part of the work.

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TESTS ON THE OPACITY AND HIDING POWER OF PIGMENTS¹

By G. W. THOMPSON

In the discussion of paint problems, certain terms are often used with such different meanings that great confusion has resulted. Thus, the word "covering power" is defined in three or more different senses by Dr. Dudley in his articles in the "*Railroad and Engineering Journal*" running in the issues of 1890 to 1893; and the word "body" has so many different meanings that hardly two persons consider it as referring to the same thing. For this reason, it seemed desirable to Committee D1 of the American Society for Testing Materials that the use of these two terms should be discouraged and they have substituted two simpler terms to cover the more usual uses of these words. These terms and their definitions are as follows:

Hiding Power.—The power of a paint or paint material, as used, to obscure optically a surface painted with it.

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

Opacity.—The obstruction to the direct transmission of visible light afforded by any substance, comparison being made with sections of equal thickness. The opacity in the case of pigments should be considered as referable to their opacity in a vehicle under standard conditions.

The distinction between opacity and hiding power should be evident in the study of these definitions. Opacity refers to tests made under standard conditions; and hiding power refers to tests made of paints, etc., as they are used. The distinction becomes clearer when considered with reference to a paint, the opacity of which is measured with a standard thickness of paint, while in the case of the hiding power the thickness of the paint will vary according to the spreading rate at which the paint is applied.

In many laboratories, tests for opacity have been conducted on the assumption that what is known as the strength or tinting strength of a pigment is a measure of its opacity. From numerous tests which we have made, we have come to the conclusion that strength is only an indication of opacity, and that, working on pigments of the same composition, it is not safe to assume that the strength of the pigment is a measure of its opacity. By *strength* or *tinting strength* we mean here:

"The relative power of coloring a given quantity of paint or pigment selected as standard for comparison," which is the definition agreed upon by Committee D of the American Society for Testing Materials. Much heated discussion has appeared in the *Farben-Zeitung* during the last year or more as to whether strength is proportional to opacity. Unfortunately, these discussions are largely academic and not based on practical or accurate tests. As far as the discussions have gone, it would appear that they have not led to any definite conclusion.

Without going into the question of the tinting strength of pigments in this article, we propose to discuss a method which we have developed for the measurement of the opacity of pigments and paints and which will serve, we hope, to some extent, at least, to clear up one phase of this subject.

In developing a method for the determinations of the opacity of pigments, it has been impressed upon us that opacity should never be measured in terms of weight. This has been brought out by Dr. Dudley and by some of the disputants in the *Farben-Zeitung*, but is not as generally recognized as it should be. It seems to us that there can be no question that, in all comparisons of opacity, the relative volume of the pigment should be considered and that a standard of opacity should be based upon a definite volume of the pigment placed in a definite volume of a menstruum. The futility of comparing pigments for opacity by weight is evident where these pigments vary in their specific volumes, as most pigments of different compositions do.

In comparing pigments or paints for opacity, we are compelled to recognize that it is somewhat of a physiological problem. We really have no good means of detecting differences in light except in the

sensations they produce upon the retina of the eye. Photochemical and photoelectrical methods have not, so far, proved satisfactory. This being the case, all photometric work has to be based upon certain standards for comparison. In the case of tests for opacity, however, we have not as great difficulty in this respect as we have in the case of the ordinary photometric measurements. By the use of a single source of light and a suitable photometric bench, the opacity of a substance can be determined with a certain degree of accuracy. Following the method used by Hürter and Driffield, who worked upon photographic plates, it is possible to construct plates varying in opacity and whose opacity can be determined. It is hardly necessary to describe in detail the method to be followed for this work, and we would refer to the original article by Hürter and Driffield in the *Journal of the Society of Chemical Industry*, 9, 455 (1890).

There is, however, one difficulty which affects the determination of opacity and the preparation of standard opacity test pieces. In a one-light photometer the light is reflected so as to come from opposite directions and when properly balanced, the light should be equal at zero. By placing the object to be tested in the course of one of these beams of reflected light, the light becomes reduced and the balance of light is found at another point which gives a means of calculating the opacity of the object being tested. Unfortunately, the accuracy of the test depends upon no light being reflected by the object being tested, or that the luminosity or reflecting power of the object being tested shall be determined and applied as a correction to the opacity found.

Hürter and Driffield worked upon gelatine silver films which, apparently, they assumed had no reflecting power, or that, in their case, the reflecting power could be included by them in the opacity for the practical purposes for which tests were conducted. In the testing of white paints, however, this cannot be assumed, for, as we will show, the amount of light that is reflected is apparently very much in excess of the light that is absorbed during transmission.

According to the best information obtainable, opacity proper follows a logarithmic law known as Bouguer's Law. Nutting, in his recent "Outlines of Applied Optics"—1912, says: "Absorption during transmission follows the logarithmic law in every known case; that is, if a given layer absorbs a certain fraction of transmitted radiation, the next equal layer will absorb the same fraction." Thus, if the first layer absorbs half of the light being transmitted, the next layer will absorb half of the remainder or one-quarter of the light being transmitted; the next layer one-eighth of the light being transmitted, and so on.

To express numerically the opacity of a paint, we should define in some term the light absorbed in transmission for a standard thickness. In a paper read before the International Congress of Applied Chemistry, I suggested that this thickness be 0.1 mm. I find, however, that this thickness was too great for

the proper measuring of opacity and that it would be better to use 0.01 mm. thickness as the unit of thickness in which to express opacity. Of course, any thickness could be used, but it would be better to have a thickness that corresponds to some practical thickness of paint. I, therefore, feel that it would be better to adopt the latter thickness. In expressing the opacity it would seem to me that it should be called the "coefficient," and, having the coefficient, we can calculate the total opacity for any given thickness. We would define, therefore, the coefficient of opacity as the proportion of light, expressed in a decimal fraction of unity, absorbed during transmission through a thickness of 0.01 mm. of paint.

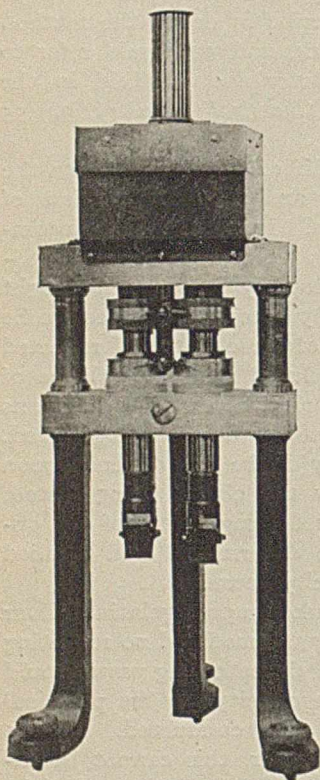


FIG. 1

(Eye-piece is shorter than that used)

We have constructed a piece of apparatus for the purpose of making these tests, which consists, first, of a photometer which will bring two fields of light into juxtaposition so that they can be compared by the eye. This photometer is placed on top of two tubes, the lower ends of which are covered with plano-plano lenses. Below these lenses are two other similar lenses. Below these are two total reflection prisms which direct light from a series of incandescent lamps up through the tubes to the eye and, by adjusting the prisms and the lamps, the light can be made to be equally sent up through the two tubes. The tubes holding the upper plano-plano lenses have micrometer milled wheels on them, so that the distance between each set of lenses can be controlled and measured. Paint placed between one set of lenses can be compared with a standard paint or with a piece or pieces of paper which have been tested on a photometer bench and the proportion of light they transmit determined. The thickness of the paint can then be varied until the amount of light transmitted matches that transmitted through the standard paint, or the test papers. The thickness of the film of the paint being tested is then read off on the micrometer. Running another test with a different opacity standard of paper or paint, two readings are obtained from which can be calculated the amount of light that is absorbed and the amount of light that has been reflected. Considering opacity as having to do only with the light that is being transmitted, and not to do with the light which is reflected from the surface of the paint, we can figure the coefficient of opacity by the following calculation:

Let a_1 = proportion of light transmitted by test paper No. 1.
 a_2 = proportion of light transmitted by test paper No. 2.
 $a_1 < a_2$.
 b_1 = thickness of paint film transmitting the same amount of light as test paper No. 1.
 b_2 = thickness of paint film transmitting the same amount of light as test paper No. 2.
 Same paint formula is used for b_1 and b_2 .
 $b_1 > b_2$.
 c = incident light = unity.
 x = proportion of incident light reflected which is independent of the thickness of the film except for very thin films.

Then $\frac{a_1}{a_2} = \frac{c - x}{c - x}$ = proportion of entering light transmitted by $b_1 - b_2$ thickness of paint, a_2 being the light entering the $b_1 - b_2$ film as it is the light transmitted by the b_2 film.

It is necessary that we give here the development of a formula for the light that passes through any number of units of thickness of paint.

L = the light passing through any number of thickness units.

S = the light absorbed by any thickness unit or units.

a = the light striking the first surface.

A = the ratio $\frac{L}{a}$

B = the ratio $\frac{S}{a} = 1 - A$.

n = the number of units of thickness.

P = the constant opacity of each unit of thickness in the form of a decimal fraction of unity.

Light passing through no unit of thickness:

$$L^0 = a = a$$

Light passing through one unit of thickness:

$$L_1 = a - Pa = a(1 - P)$$

Light passing through two units of thickness:

$$L_2 = (a - Pa) - (a - Pa)P = a(1 - P)^2$$

Light passing through three units of thickness:

$$L_3 = \{(a - Pa) - (a - Pa)P\} - \{(a - Pa) - (a - Pa)P\}P = a(1 - P)^3$$

$$L_n = a(1 - P)^n$$

$$\frac{L_n}{a} = A_n$$

$$\therefore A_n = (1 - P)^n \quad \text{General formula}$$

$$B_n = 1 - A_n = 1 - (1 - P)^n$$

From the formula $A_n = (1 - P)^n$, where A_n is the proportion of entering light transmitted, P is the opacity of unit thickness in terms of decimal of unity and n is the number of units of thickness.

$$\frac{a_1}{a_2} = (1 - P)^{b_1 - b_2}$$

$$P = 1 - \sqrt[b_1 - b_2]{\frac{a_1}{a_2}}$$

From formula $B_n = 1 - (1 - P)^n$ where B_n is the proportion of entering light absorbed:

$$B_{b_2} = I - \left[I - \left(I - \sqrt{\frac{a_1}{a_2}} \right) \right]^{b_2}$$

$I - x$ = proportion of incident light entering b_2 film.

$$B_b (I - x) + x + a_2 = I$$

$$\left\{ I - \left[I - \left(I - \sqrt{\frac{a_1}{a_2}} \right) \right]^{b_2} \right\} (I - x) + x + a_2 = I$$

from which

$$x = \frac{I - a_2 - \left\{ I - \left[I - \left(I - \sqrt{\frac{a_1}{a_2}} \right) \right]^{b_2} \right\}}{I - \left\{ I - \left[I - \left(I - \sqrt{\frac{a_1}{a_2}} \right) \right]^{b_2} \right\}}$$

$$x = I - \frac{a_2}{\left[I - \left(I - \sqrt{\frac{a_1}{a_2}} \right) \right]^{b_2}}$$

This formula looks rather complicated, but, in practice, and by the use of logarithmic tables, the work is more simple than it seems on first inspection.

The apparatus to which I refer reads to the one thousandth of an inch and, preferably, should have been constructed with the millimeter scale. It is a simple matter, however, to make conversions into the mm. scale.

In making these calculations, it is to be observed that, the comparison of the pigments having been made between glass surfaces, the amount of light reflected from the adjacent surfaces of a paint would probably be different from the light reflected from the surface of paint which is adjacent to air. This is a controlling reason why the reflected light should not be considered in calculating the coefficient of opacity.

In testing pigments for their coefficients of opacity, we have followed the plan of mixing these pigments with linseed oil on a standard formula of 25 per cent. by real volume of pigment and 75 per cent. by volume of oil. In some cases, as, for instance, in the case of zinc oxide, this may be too large a volume of pigment, to handle conveniently in the apparatus; but, if trouble is experienced, a different formula can be used, comparing it with another standard pigment on this changed formula.

This apparatus is somewhat new and we have not as many results to report of work done upon it as could be desired, and what we present here is simply for information; and, so that the subject may be more generally studied, we present here some determinations made in this apparatus, working on a number of white pigments. It is not to be supposed that these tests represent average pigments or that the results presented are for the purpose of condemning any of the pigments tested. It is very probable that the pigments upon the market, of the kind described, vary considerably from the figures presented here. The coefficients of opacity and the light reflected by

the different white pigments, tested on the formula given above, are shown.

The values for P are the coefficients of opacity as defined above. The reflection is the proportion of incident light reflected and is expressed in decimals of unity.

Pigment.	Coefficient of opacity P	Reflection*
White lead—Dutch.....	0.0671	0.935
White zinc—American process....	0.0794	0.956
White zinc—French Pr.....	0.0645	0.964
Lithopone.....	0.0578	0.947
Calcium carbonate.....	0.0136	0.969
Basic lead sulphate.....	0.0813	0.927
China clay.....	0.0190	0.823
Asbestine.....	0.0090	0.859
Calcium sulphate.....	0.0030	0.856
Silica.....	0.0102	0.793
Barytes.....	0.0114	0.856

This work was done in the research laboratory of the National Lead Co., much of it having been accomplished with the assistance of one of my associates, Mr. R. L. Hallett, to whom I tender thanks.

AN APPLICATION OF THE ELECTRIC RESISTANCE FURNACE TO THE DETERMINATION OF OXYGEN IN IRON AND STEEL

By R. H. McMILLEN

Received January 6, 1913

The fact that iron and steel always contain more or less oxygen has long been known, and about thirty years ago, Ledebur¹ called attention to it and gave a method for its determination. It is only recently, however, that the requirements in the manufacture of high-grade steels have become so exacting that the determination of oxygen in steel and other materials has come to be one of the routine determinations required of a steel laboratory.

The Ledebur method, which is well known, consists in heating the sample of iron or steel in nitrogen to remove all moisture without oxidizing it, then reducing the oxides at a red heat by hydrogen and absorbing and weighing the resultant water. Cushman² has shown that the drying of the sample in nitrogen is unnecessary, his results being but slightly higher than those by the original method. When used with electric resistance furnaces, this method is very satisfactory for the determination of oxygen in iron and steel, tungsten,³ and other non-volatile metals. Even this method, however, will fail to show all the oxygen in metals containing oxides of silicon, vanadium, titanium, and other elements whose oxides are not reduced below 950° C.⁴

The following modification of the Ledebur method has been found to give most satisfactory results:

APPARATUS

The apparatus consists of two electric resistance

¹ Sauerstoffbestimmung im schmiedbaren Eisen, *Stahl u. Eisen*, 2, 193.

² "The Determination of Oxygen in Iron and Steel," *THIS JOURNAL*, 3, 372.

³ Tungsten powder often contains a rather large percentage of oxides. Some commercial samples investigated by the writer recently have shown an oxygen content corresponding to 12 per cent. WO₃. It is probable, however, that the whole of the oxygen is not combined with the tungsten.

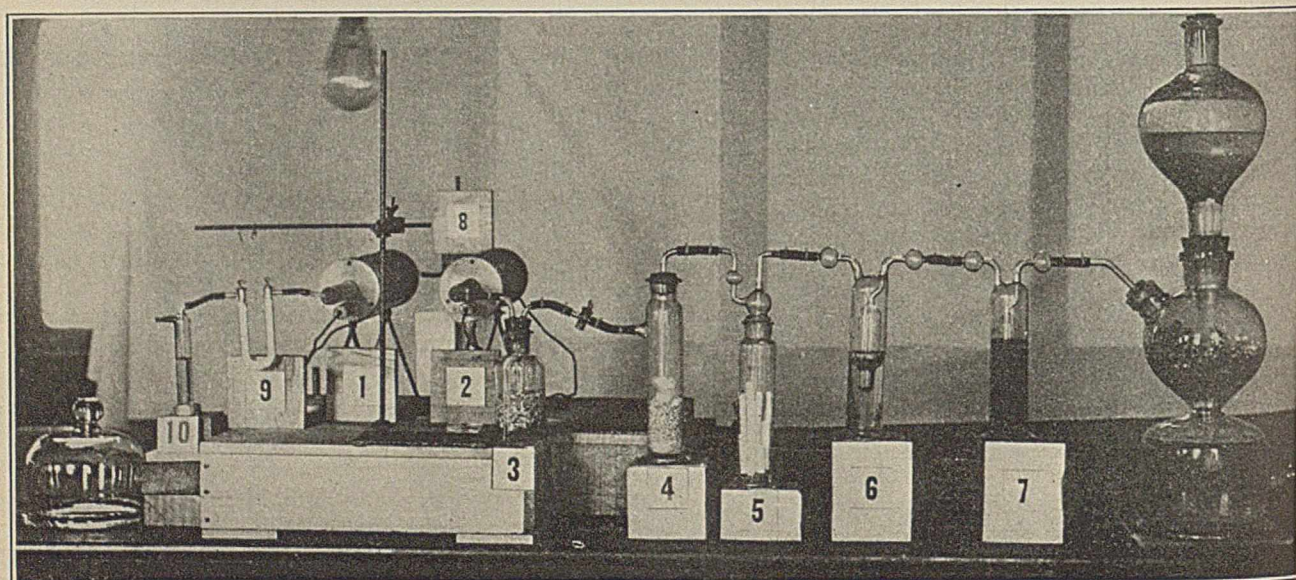
⁴ See "The Determination of Oxygen in Iron and Steel, by Reduction in an Electric Vacuum Furnace," by W. H. Walker and W. A. Patrick, *THIS JOURNAL*, 4, 799.

furnaces, such as are employed in many steel laboratories for combustion carbon determinations and capable of maintaining a temperature of 950°C . They are designated as No. 1 and No. 2 in the illustration. Both furnaces are equipped with heavy-walled, fused quartz tubes $\frac{7}{8}$ inch inside diameter by 24 inches long. The function of furnace No. 1 is to heat the sample under investigation, while that of No. 2 is to heat the hydrogen so that it may combine with any oxygen that may be carried over from the hydrogen generator. Several spirals of platinum gauze are placed in the quartz tube of this furnace. The quartz tubes of these furnaces are connected in the rear by a U tube (not shown in figure) having close-fitting glass stopcocks. This U tube is filled with phosphorus pentoxide opened by small glass beads. The phosphorus pentoxide absorbs any water which may be formed in the tube of furnace No. 2, and insures absolutely dry hydrogen to pass over the sample in furnace No. 1. The front end of the quartz tube in No. 2

so that they be free from rust or foreign oxides. In the case of iron or steel samples both the fine and coarse drillings are rejected, only those between twenty (20) and thirty (30) mesh being used. These are dried for at least one hour over concentrated sulfuric acid before using. Samples of tungsten powders are dried to constant weight in the drying oven at a temperature of 105°C .

PROCEDURE

Twenty-five (25) grams of the prepared drillings are weighed into the dried porcelain boat and placed in the tube of furnace No. 1. Connection is made to the weighed U tube, No. 9, through which, just previous to drying for fifteen (15) minutes and to weighing, hydrogen has been passed for ten (10) minutes. Guard tube No. 10 is connected. Hydrogen is allowed to pass through the whole apparatus at a rapid rate for fifteen (15) minutes. For the first run it is advisable to allow the hydrogen to sweep through the whole apparatus for thirty (30) minutes to insure complete



furnace is connected to the drying and purifying train leading from a hydrogen generator. No. 3 contains small pieces of pumice stone saturated with concentrated sulfuric acid, No. 4 soda lime, No. 5 stick potassium hydrate, No. 6 a 50 per cent. solution of pyrogallol made alkaline with potassium hydrate. Hydrogen is generated in a sixty-four (64) ounce Kipp apparatus by the action of chemically pure hydrochloric acid on pure mossy zinc. The water formed by reduction of oxides in the sample is absorbed in U tube No. 9 of same construction as No. 8, and also filled with phosphorus pentoxide opened with small glass beads. A guard tube, No. 10, is attached to No. 9 and contains concentrated sulfuric acid. A small wash bottle of the Drexel form is used for this purpose. Porcelain boats of sufficient size to hold at least twenty-five (25) grams of the sample are employed.

PREPARATION OF SAMPLE

Great care must be taken in preparing the samples

expulsion of oxygen from the train and tubes. The train and quartz tube of furnace No. 2 can be kept constantly filled with hydrogen by closing the cocks of U tubes No. 8 whenever the flow of hydrogen is interrupted.

The electric current is turned on and continued for one hour after the maximum temperature has been reached. During this time the flow of hydrogen is cut down to about seventy (70) bubbles per minute, this rate being maintained until U tube No. 9 is removed. At the end of the hour the current is turned off and furnaces allowed to cool, accelerating the cooling with a blast of compressed air. When the quartz tubes in the furnaces show no visible redness, the cocks of U tube No. 9 are closed and a pinchcock is inserted over the rubber tube connecting U tube No. 9 to the quartz tube of furnace. In this manner oxygen is kept from the heated tube, thereby avoiding danger of explosion. U tube No. 9 is disconnected and carefully wiped with a soft, dry cloth then desiccated over concentrated sulfuric acid for fifteen min-

utes and finally quickly weighed. Weight of water, after deducting blank, multiplied by 0.8888 divided by 25 equals oxygen.

A blank should be run frequently, adhering to all details as to time of heating furnaces, desiccating U tube, etc. Usually the blank found varies between 0.0015 and 0.0025 gram.

For samples of tungsten powder the same procedure is carried out except that a smaller sample is taken varying from one to ten grams according to the amount of oxygen present.

The following table gives results on several samples in duplicate by the above described procedure:

No.	Oxygen					
	C	Mn	S	P	Si	
1 Crucible steel.....	1.15	0.31	0.018	0.011	0.22	0.039 0.037
2 Crucible steel.....	1.17	0.31	0.015	0.010	0.22	0.035 0.035
3 Crucible steel.....	1.14	0.33	0.016	0.009	0.21	0.044 0.045
4 ¹ Basic open hearth steel...	0.07	0.06	0.019	0.008	0.08	0.113 0.115
5 Basic open hearth steel...	0.08	0.22	0.016	0.008	0.01	0.079 0.072
6 Swedish wrought iron...	0.06	0.17	0.019	0.012	0.02	0.345 0.353
7 Domestic wrought iron...	0.69	trace	0.009	0.007	0.06	0.069 0.076
8 Domestic wrought iron...	0.73	..	0.009	0.007	0.06	0.090 0.089
9 Acid open hearth steel...	0.36	0.69	0.040	0.046	0.03	0.043 0.042
10 Bessemer steel.....	0.46	0.72	0.041	0.095	0.09	0.058 0.060
11 Tungsten powder.....	2.57 2.57
13 Tungsten powder.....	1.37 1.34
14 Tungsten powder.....	0.55 0.56
15 Tungsten powder.....	1.02 1.05

¹ This sample fractured badly in rolling.

Numbers 1, 2 and 3 were three ingots made under as nearly the same conditions as possible. It is not intended that the above table should be typical as to the oxygen content that exists in the different classes of steel. In many samples of crucible steel it is much lower than those cited.

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THE VOLUMETRIC DETERMINATION OF MANGANESE IN ROCK, SLAGS, ORES AND SPIEGELS

By F. J. METZGER AND L. E. MARRS
Received November 1, 1912

A new and accurate method for the determination of manganese and its application to the analysis of iron and steel has been published by us in THIS JOURNAL (3, 333). The method has since been applied to rock, slags, ores, and spiegels and it is the purpose of this paper to report on these.

Analyzed samples of rocks and of a manganese ore were furnished by W. F. Hillebrand, of the Bureau of Standards. We desire to express our gratitude to Dr. Hillebrand for this material assistance and for the kindly interest he has shown during the progress of our work.

Rock.—Here the manganese content is apt to be very low and for accurate work a portion of from two to five grams should be taken for analysis. Place the weighed portion in a platinum dish; add 5–15 cc. dilute sulfuric acid (1 : 2) and boil; add 5–15 cc. hydrofluoric acid and boil until the rock is completely decomposed. Add 5–10 cc. dilute nitric acid (1 : 1) and 2 or 3 cc. of concentrated sulfuric acid; remove from the flame and add about one gram ammonium persulfate in small portions: when evolution of gas has ceased, evaporate to fumes of sulfur trioxide,

cool, add 50 cc. water, boil and cool. Transfer to a wax beaker, add 5 grams ammonium fluoride and 25 cc. hydrofluoric acid (making a total volume of about 100 cc.) and titrate to a permanent pink color with potassium permanganate solution (approximately $N/30$).

The value of the permanganate in terms of iron multiplied by 0.78682 gives the value in terms of manganese, or by 1.01601 in terms of MnO.

Slag.—Weigh out 0.2–1.0 gram and treat as in rock unless the manganese content is high. If more than about 20–30 mg. of manganese is present in the solution titrated, a brown color will appear toward the end of the titration, but, with a very little experience, as much as 60 mgs. may be titrated with accuracy using a $N/10$ (approx.) permanganate solution. With high percentages of manganese, the titration of an aliquot part of the solution is much more accurate than weighing out exceedingly small amounts. It has been found best to titrate with a volume of about 150 cc. containing about 60 mgs. of manganese when more than 40 per cent. of manganese is to be determined.

If much manganese is present in the solution, oxidized manganese compounds may appear after the addition of the nitric acid to the mixture; the authors have found, on several occasions, a strong permanganate color, on several occasions, a strong permanganate color on taking the mixture to fumes of sulfur trioxide. *When this occurs*, cool; add 50 cc. water; cool again; add hydrogen peroxide (drop by drop) until the color disappears; boil about ten minutes, cool, and titrate as usual.

Ores.—Pyrolusite: Dissolve 0.5–1.0 gram of the ore in a casserole, using as small a quantity of dilute hydrochloric acid (1 : 1) as possible. Add 15 cc. dilute sulfuric acid (1 : 2) and evaporate to fumes of sulfur trioxide.¹ Cool and add 10 cc. dilute nitric acid (1 : 1) and about 1 gram of ammonium persulfate (have the casserole covered). After evolution of gas has ceased, remove cover and take to fumes of sulfur trioxide. Cool, dilute with water, cool again, transfer to a 250 cc. flask and dilute to the mark. Take an aliquot portion (preferably not less than 0.1 gram of the original ore) and titrate in a volume of about 150 cc., containing 5 grams ammonium fluoride, 10 cc. dilute sulfuric acid (1 : 2) and 25 cc. hydrofluoric acid.

Ores, Slags, etc., Insoluble in Hydrochloric or Nitric Acid.—Proceed as in rock, using peroxide treatment if necessary.

Spiegels (and Ferromanganese).—Weigh out 0.2–1.0 gram and dissolve in 5–10 cc. dilute nitric acid (1 : 1) in a covered casserole; cool slightly and add 1 gram ammonium persulfate; when action has ceased, remove cover, add 15 cc. dilute sulfuric acid (1 : 2) and evaporate almost² to fumes of sulfur trioxide; cool, add 50–100 cc. water;³ heat until ferric salts are

¹ All hydrochloric acid must be removed as titrations made with even small amounts of HCl were decidedly inaccurate.

² Nitric acid up to 2 cc. concentrated acid in a volume of 150 cc. has no effect on the titration.

³ If any oxidized manganese appears here, treat with hydrogen peroxide as described under *Slag*.

dissolved; cool, place in 250 cc. flask, dilute to mark and take aliquot portions for titration (see conditions under Pyrolusite). For all titrations of spiegels use N/10 (approx.) permanganate solution.

The subjoined table gives results of analyses of the various products.

Sample	Manganese found ¹	Manganese found by other methods	
	Percentage MnO	Percentage MnO	Later colorimetric ⁴
Rock A ²	0.040	0.04	
Rock 1.....	0.246	0.16 ³	
Rock 2.....	0.316	0.28 ³	
Rock 3.....	0.259	0.18 ³	
Rock 4.....	0.278	0.28 ³	
Rock 5.....	0.346	0.22 ³	
		Original gravimetric ³	Later colorimetric ⁴
Rock 6.....	0.23	0.16	0.18
Rock 7.....	0.19	0.10	0.13
Rock 8.....	0.09	0.07	0.06
Rock 9.....	0.30	0.26	0.25
Rock 10.....	0.26	0.20	0.19
Rock 11.....	0.21	0.13	0.19
Rock 12.....	0.11	0.08	0.08
Rock 13.....	0.26	0.22	0.23
Iron slag 1.....	15.91	15.88	
	Percentage Mn	Percentage Mn gravimetric phosphate	
Spiegel 1.....	11.09	11.10	
Spiegel 2.....	21.01	20.99	
Spiegel 3.....	30.55	30.49	
Ferromanganese.....	80.10	80.22	
Manganese ore ⁵ dried at 122° C.....	57.09	B. of S. certificate	
	57.07	High	56.63
	57.11	Low	56.15
		Average	56.36

¹ The results expressed here are the averages of two or more closely agreeing determinations.

² This is a sample of Bureau of Standards argillaceous limestone, analysis by Hillebrand and Walters. See *Jour. Am. Chem. Soc.*, 28, 223.

³ These results were obtained by W. F. Hillebrand some years ago. Concerning them, Dr. Hillebrand writes: "The manganese was determined with the usual care bestowed on rock analyses, but not in duplicate." And again, "My determinations on these particular rocks were made before I began to determine the small amounts that pass into the filtrates with the lime and magnesia. There was, too, always the possibility, in spite of a basic acetate separation, that a little had not been separated from the Fe and Al."

⁴ "These tests were made with some care, by the color method, correcting for the influence of color due to the iron content of the rocks."—W. F. H.

⁵ Bureau of Standards analyzed "Sample No. 25."

The method has been used successfully in this laboratory for some time. Whereas a little experience is required to accurately determine the end point in titrating large amounts of manganese (40 to 60 mg.), the end point is sharp and distinct and the results are very accurate in determining small amounts of manganese.

The difficulties encountered in determining small amounts of manganese in rock and similar materials are known to analysts and it is believed that the method here described overcomes these difficulties.

It is also believed that the principle involved in the above method may explain some of the discrepancies arising in the determination of ferrous iron in rock.

ANTISEPTIC TESTS OF WOOD PRESERVING OILS¹

By A. L. DEAN AND C. R. DOWNS

The materials commonly employed for impregnating wood for the purpose of preventing its decay fall readily into two classes—soluble salts and hydrocarbon oils. The most widely used member of the first group is zinc chloride, and of the second, coal tar creosote. Ever since the introduction of this last named material by Bethell in 1838 it has been employed in constantly increasing amounts, and today creosoting—properly performed—is regarded as the most effective method of timber preservation.

In recent years the large demand for coal tar creosote and the rather high cost of the treatment with the amounts considered necessary, have led to the use, openly and otherwise, of other materials. Thus the heavy asphaltic petroleum oils have been tried to some extent, notably in the treatments by the Santa Fe railroad where sufficient of the oil has been injected to render the wood well-nigh waterproof. The oil distilled from the tar resulting from the manufacture of carburetted water gas has been used to a considerable extent, but since its value was uncertain it has been regarded as an adulterant or substitute for the oils distilled from coal tar. Water gas tar shows many points of similarity to coal tar, and the creosote oil distilled from it is very like that distilled from coal tar, although it contains neither the phenols nor the nitrogenous bases characteristic of the latter. Inasmuch as large quantities of water gas tar are produced at the gas works in the United States, and the creosote distilled from it might readily be had in substantial amounts, it is important to arrive at a sound estimate of its value as a timber preservative.

The qualities commonly desired in a wood preserving oil are freedom from loss by volatilization, solution or chemical change, and a marked toxicity to wood-rotting fungi and the animals which destroy timber.

In volatility, solubility and chemical inertness water gas tar creosote compares favorably with the oils from coal tar; the relative antiseptic powers of the two classes of oils are less readily determined. The present communication outlines the results of a laboratory study of the antiseptic powers of oils prepared from coal tar and water gas tar, and is designed to assist in arriving at a proper estimate of the place that water gas tar oils should occupy in timber preservation.

The value of water gas tar creosote as a wood preservative has been the subject of some controversy, but as yet the amount of reliable data has not been large. Practical tests on a commercial scale giving the results of the test of time under service conditions have not been carried out. Where the material has been used it has usually been employed in mixture with coal tar creosote, sometimes without the consumer's knowledge. The result has been that in the absence of reliable information consumers have preferred to rely on coal tar creosote of the value of which they were certain.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

Alleman¹ has studied the character of the oils remaining in timbers which, after being treated with coal tar oils, have been many years in service. The results show that the low-boiling oils present in creosote disappear after a number of years of service, and the tar acids or phenols are no longer present. There has been in recent years a growing tendency to regard these high-boiling hydrocarbon oils such as Alleman found remaining in his well preserved timbers as the most valuable constituents of creosote oils.

During 1911, J. M. Weiss² presented two papers to the New York Section of the Society of Chemical Industry, dealing with the antiseptic value of the oils and tars used in timber preservation. These papers showed the relative antiseptic value of coal tar oils and water gas tar oils under the conditions of Weiss' experiments, as well as furnishing some information on the relative values of the different tar oil constituents. These papers furnish the most important experimental evidence of the antiseptic powers of the different oils. The work of Weiss showed that coal tar creosote was many times as toxic to the organisms used in his experiments as the water gas product, and that the lower boiling coal tar oils were distinctly more antiseptic than the heavy high-boiling ones.

Two criticisms may be made of the methods employed by Weiss. The first, and less important, being that the fungi used by him to test the antiseptic powers of the materials experimented on by him were not wood-destroying fungi and their powers of resistance to various agents might not be the same. A much more serious objection to his results depends upon the method employed in preparing the media containing the oils to be tested. These are for the most part insoluble in water and, being heavy, sink rapidly to the bottom of the containing dishes, so that a uniform distribution of the oil is not effected, and the cells of the fungi may not come in contact with it. It is apparent that oils containing water-soluble constituents would partially dissolve and prove more antiseptic than the more insoluble oils. It might readily be that the relatively greater antiseptic power of the lighter coal tar oils was partly due to solubility of the phenols present in them, the toxic power of which is well known. It would seem that a much fairer idea of the antiseptic power of the oils tested could be gained if they were uniformly distributed throughout the culture medium so that the fungus must come in contact with them.

The organism used in the experiments to be described was *Polystictus versicolor* obtained in pure culture from wood decaying through the action of this fungus and bearing masses of its sporophores on the surface. Numerous cultures were kept in the laboratory on small blocks of sterilized *Liriodendron* wood on which it grew readily, and which it reduced to about the specific gravity and strength of pith in the course of a few months. There was no doubt of the purity of the cultures nor of the powerful attack of the fungus

¹ Gellert Alleman, *Circular 98*, Forest Service of the U. S. Department of Agriculture, May, 1907.

² J. M. Weiss, *J. Soc. Chem. Ind.*, Feb. 28, 1911, p. 190, and Dec. 15, 1911, p. 1348.

on the wood. This species was used because of the readiness with which it may be isolated in pure cultures which grow vigorously under laboratory conditions, and also because it is one of the most important enemies of structural timber in the United States. Von Schrenck¹ says of this species: "Of all the fungi which grow upon the deciduous species of woods after they are cut from the tree, the most widely distributed and in many respects the most destructive is *Polystictus versicolor*. . . . On account of its wide geographical range and its ability to grow on and destroy so many different kinds of wood it should be regarded as the most serious of all the wood-rotting fungi which attack the dead wood of broadleaf trees. It is the fungus which destroys probably 75 per cent. or more of the broadleaf timber used for tie purposes."

Inoculations into the media to be tested could not be conveniently made from cultures growing on wood, and transfers were therefore made to prepared agar from which the fungus could be readily cut and small masses of the mycelium transferred by the use of a small piece of platinum foil set in a glass handle

The culture media were prepared in the following manner: Ordinary white beans (*Phaseolus vulgaris*) were germinated in a dark place until several inches high. The seedlings were then ground up in a meat chopper and a boiling water extract of them made. Due to the chemical changes characteristic of the process of germination some of the starch of the beans is hydrolyzed to dextrans and sugar, and much of the nitrogen present as the proteins of the seeds appears as soluble cleavage products in the seedlings. One-half of one per cent. of cane sugar and a like quantity of asparagin were added to the germinated bean extract to supply further nourishment. This medium was then stiffened by the addition of 1.5 per cent. of agar agar, and 10 cc. portions of it pipetted hot into 22 mm. test tubes, plugged with cotton and sterilized.

A five-gram portion of each of the creosote oils to be tested was weighed out into a mortar containing an equal weight of powdered gum arabic and the two rubbed well together. Water was then added a little at a time with constant grinding, yielding an emulsion containing as the emulsifying agent a carbohydrate material similar to the agar agar of the medium. The emulsion was diluted with water to 100 cc., making a 5 per cent. emulsion which would not separate even after several months of standing.

Portions of these five per cent. emulsions were measured into the 10 cc. portions of the sterilized agar medium with a pipette graduated to hundredths of a cubic centimeter. As a rule three test tubes of each strength were prepared in order to check the results. The agar was then melted and the tubes well shaken in order thoroughly to mix the emulsion with the medium, and then quickly cooled under cold water in a slanting position. In this way the oil was uniformly distributed throughout the medium in the form of finely divided globules and held permanently in position by the solidification of the agar.

¹ Von Schrenck, *Bull.* 149, Bureau of Plant Industry of the U. S. Department of Agriculture, p. 53.

In the first series of tests the oils used were a very good grade of commercial coal tar creosote, a water gas tar creosote made in the laboratory by taking the fraction distilled from 170° to 340° C. from a sample of water gas tar of known origin, and a sample of pressed anthracene oil. The results of the fractional distillation of the two first samples are given in the table below:

TEMPERATURE DEGREES C.	COAL TAR CREOSOTE PER CENT.	WATER GAS TAR CREOSOTE PER CENT.
... 170	0.2	5.5
170 205	6.3	4.5
205 240	30.7	35.5
240 300	21.3	32.5
300 320	9.1	6.0
320 340	13.5	..

The coal tar oil contained 8 per cent. of tar acids. The anthracene oil was a commercial product, 50 per cent. of which distilled between 250° and 350° C. The solids had been pressed out, leaving it liquid at room temperatures.

The strengths of coal tar creosote tested varied by 0.05 per cent. increments from 0.05 per cent. to 0.35 per cent., and of the other two oils from 0.05 per cent. to 0.75 per cent.

The results of this preliminary series indicated an inhibition point for the fungus with 0.25 per cent. of coal tar creosote, 0.40-0.45 per cent. of the water gas tar creosote, and over 0.75 per cent. for the pressed anthracene oil. In the case of the last named material the growth became progressively weaker, but was not entirely inhibited at the highest concentration tried.

One serious difficulty developed in the tests. In transferring the fungus mycelium to the test tubes it was necessary to cut out a small piece of the agar of the stock culture and it was almost impossible to tell whether the fungus was growing slightly on the creosoted agar or whether all the growth was derived from the small piece of transferred medium. This led to some uncertainty as to the precise point at which growth was inhibited. In the second series, this was remedied by cutting out a small piece of the medium to be inoculated with a sterile platinum foil, laying the cut out piece over to one side, placing the transferred mycelium and agar from the stock culture in the cavity, and then replacing the piece of creosoted medium on top of the transferred material. In this way the mycelium used for inoculation was buried within the mass of material to be tested and if it grew up through it and vegetated at the surface there could be no question that the antiseptic was insufficient to prevent the growth of the fungus. The control cultures were made in the same manner.

The too rapid drying out of the cultures noticed in the first series was prevented in the second by placing them in a large glass walled case with a water-saturated atmosphere.

Since the fungus used in the first series might have had its vitality somewhat impaired by being kept so long in artificial cultures, new samples of wood decaying through the action of the organism were found and fresh, pure cultures prepared and used for inocu-

lating the second series of tests. The following oils were tested:

- A. Coal tar creosote No. 1.
- B. Coal tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from 200° to 350° C., from a sample of coal tar; since there was a considerable separation of naphthalene in this sample on cooling to room temperature, which rendered it impossible to make a satisfactory emulsion, the solids were filtered off.
- C. Water gas tar creosote No. 1.
- D. Water gas tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from water gas tar between 200° and 350° C., yielding a sample somewhat heavier than the No. 1 and comparable in boiling range with coal tar creosote No. 2.
- E. The same sample of pressed anthracene oil used in the first series.
- F. Coal tar creosote No. 1, washed with alkali until free from tar acids and then washed with water.
- G. A portion of F. with the tar bases removed by treatment with sulfuric acid, and washed with water.

An attempt was made to make emulsions with anthracene and naphthalene for antiseptic tests in the manner described above for the oils, but it was found impossible to make satisfactory emulsions. The attempted stock emulsions of these materials containing about 5 per cent. of the hydrocarbons stood for some time in the laboratory and it was noted that a mold growth appeared on the surface. The naphthalene and anthracene had settled to the bottom. This observation would tend to support the statement made by Weiss that these materials were not antiseptic up to 10 per cent. This conclusion seems not to be wholly justified, however, because the mold was not in contact with the hydrocarbons.

The results of the tests in the second series were as follows:

SAMPLE	INHIBITION POINT PER CENT.
A. Coal tar creosote No. 1.....	Below 0.1
B. Coal tar creosote No. 2.....	0.1
C. Water gas tar creosote No. 1.....	0.4
D. Water gas tar creosote No. 2.....	0.35
E. Pressed anthracene oil.....	Above 0.85
F. Sample A. minus the phenols.....	0.30
G. Sample A. minus the phenols and tar bases.....	Above 0.6

In the case of sample E there was a gradual weakening of the growth from 0.2 per cent. to 0.85 per cent. which was the highest concentration tried, and a similar state of affairs developed in the tests of sample G, the highest strength of which was 0.6 per cent. Of the two, cultures with sample E were slightly the more vigorous.

From these results it is evident that coal tar creosote is a stronger antiseptic than water gas tar creosote, and that water gas tar creosote is distinctly more effective than the liquid oils of the anthracene fraction of coal tar. The greater value of the coal tar oil appears to depend upon the presence of the tar acids and especially upon the tar bases. It is interesting to note that the water gas tar creosote was almost identical in antiseptic power with the coal tar oil with its tar acids removed.

The work of Alleman cited indicated that the oils remaining in wood treated with coal tar creosote are almost free from tar acids after a few years of service, and that under conditions allowing evaporation the lighter hydrocarbons are nearly all lost. Loss of antiseptic power from the disappearance of the tar acids cannot take place with water gas tar oils, since they are free from phenols in the beginning.

Since the amount of creosote injected into wood is commonly 10 pounds per cubic foot or more, it would appear that the difference in antiseptic value between coal tar oils and water gas tar oils is not of great significance, especially in view of the probable disappearance of the tar acids from the wood treated with coal tar creosote.

On the basis of such data as we have it seems justifiable to conclude that the oils distilled from water gas tar have a distinct value as wood preservatives, and that there is no reason why they should not be purchased and used under their own names with no attempt to masquerade as coal tar products.

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THE OXYGEN ABSORPTION TEST FOR LINSEED OIL¹

By HANS MANNHARDT

This subject has received considerable prominence in this country through a report by a sub-committee on paint oils submitted at the Atlantic City meeting of the American Society of Testing Materials last July. The report covers twelve pages, and to any one taking the time to compare the results of the four experimenters, it must be at once apparent that either the method is not a quantitatively reliable one, or that some essential requirement has been overlooked; their results are to be found in the "1911 Proceedings."

I will quote a few classic and correct results from the standard work on drying oils by Andrés, English translation published by Scott, Greenwood & Co., in 1901, where extensive citation is made of Weger's and Lippert's results in the changes in weight which thin films of various oils undergo when exposed to the air on glass plates. Weger's glass surfaces were about 15 square inches in area and on these surfaces he applied weights of oil varying, if possible, only between 25 and 50 milligrams. His results in a condensed form follow:

	Time of drying to maximum change in weight	Per cent. maximum change in weight
Linseed oil, Artists'.....	8 days	17.0
Linseed oil, Artists', heated to 210° C....	5 days	15.5
Linseed oil, English, bottled 5 years.....	3.5 days	19.7
Linseed oil, East Indian seed:		
Raw.....	6 days	17.3
Heated to 150° C.....	6 days	17.0
Cold blown.....	8 days	16.7
Linseed oil, East Indian seed:		
Cold blown, 25 hours }.....	5.5 days	8.2
Hot blown, 25 hours }		
Linseed stand oil.....	18 days	11.1
Litharge boiled linseed oil.....	16 hours	14.6
Linseed oil and 2 per cent. lead manganese resinates (no heat used).....	8.5 hours	17.5
Rosin oil without driers.....	48 days	loss 26.5
Rosin oil (6½ per cent. lead and manganese resinates added at 120° C.).....	6.5 days	gain 25.7
Wood oils, raw, purity not vouched for....	3 to 8 days	+14 to +17
Hemp seed oil, raw.....	4 days	13.6
Poppy seed oil, raw.....	6.5 days	13.4

Looking over the tables in the "1911 Proceedings," I find that the glass area to be covered with a film of drying oil was approximately 35 square inches. The

¹ Read before the Chicago Section of the American Chemical Society, March, 1912. Revised by the author.

several experimenters used weights of oil varying between the following limits:

	Grams
A.....	0.0774 to 0.4011
B.....	0.2877 to 0.9498
C.....	0.2934 to 0.8812
D.....	0.1711 to 2.7318

On the basis of Weger's results they should have used

0.062 to 0.150 gram.

Small wonder that their results were erratic!

You will notice that Weger was successful in drying a film of rosin oil. On page 187 of the "1911 Proceedings" we find statements of three of the experimenters that their films of rosin oil and drier would not set hard. Furthermore, only two of the experimenters found any gaining in weight. The fourth experimenter did not report. Now, W. Pritchard,² mentions an XL rosin oil with "rather remarkable drying properties." I also find that thin films of "first run" rosin oil can be caused to set into a non-tacky film by the use of a proper amount of drier, while "second run," "third run" and "fourth run" oils did not appear suitable.

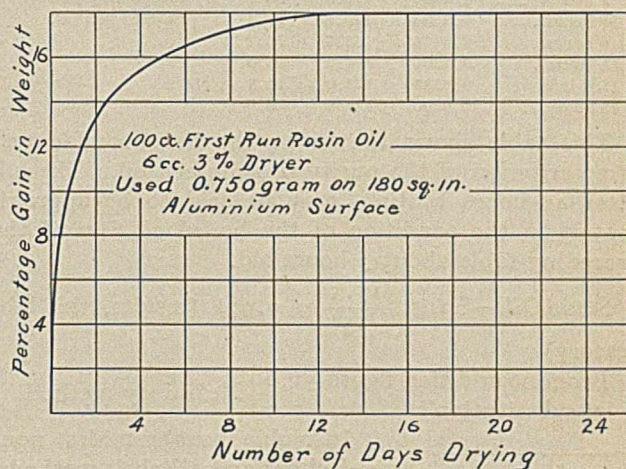


FIG. A

Apparently each redistillation decreases the suitability of the product so that "first run" is at once the cheapest and the most suitable for use in paint vehicles.

That is about all the discussion required by those twelve pages of results in the "1911 Proceedings."

Let us now see what recent literature has to say about the value of the determination of the gain in weight of a film of linseed oil; and in this connection I have selected data bringing out fully the relationship between oxidation by oxygen and by halogen.

Farben-Zeitung, October 1, 1910, page 17, states as follows: "The Hübl iodine values usually vary between 170 and 200 for raw linseed oils, however:—

	Sp. gr.	Acid value	Sapon. value	Unsat. value	Hexabromides	Hours drying	Gain in weight	Iodine value
Calcutta.....	0.931	3.1	194.5	1.5	25.2	80	18.0	164.5
La Plata.....	0.932	2.7	193.2	1.7	24.1	85	19.1	161.1
La Plata.....	0.932	2.9	190.4	1.2	22.3	83	18.4	160.2

¹ J. S. C. I., May 15, 1912, p. 420.

This worker apparently used a standardized method for his oxygen absorption test. The last two columns are most vital. I quote these data so fully on account of the low iodine values shown by the three oils, in spite of which fact they appear normal in the gain-in-weight column.

Chem. Revue der Fett u. Harz industrie, 1910, p. 260:

	Per cent. gain in weight	Iodine number.	
Original	153.8	18-hour Hübl method, 98 per cent.
2 hours...	5.4	131.6	glacial acetic acid used as solvent for the films of boiled linseed oil.
4 hours...	10.2	105.0	
6 hours...	16.8	73.9	
8 hours...	17.9	47.3	
10 hours...	18.5	26.9	
12 hours...	18.6	(a)	

(a) Not completely soluble in the solvent.

This table shows the saturation of the double linkages by oxygen accurately portrayed by the decreasing iodine values.

Jour. Soc. Chem. Industry, Mar. 31, 1911, p. 344, Harry Ingle.

	Specific gravity	Iodine value	Hexabromides	
Original oil...	0.9315	179.5	35.3	Oil heated in an open enamelled pan at 195° to 200° C.
2 hours.....	0.9350	175.5	30.7	
4 hours.....	0.9383	170.0	27.4	
6 hours.....	0.9418	165.0	26.2	
11 hours.....	0.9501	154.0	16.0	
15 1/2 hours...	0.9583	145.0	10.5	
43 hours.....	0.9800	121.0	0.9	

This table shows that even the hexabromide test is no criterion of the purity of a linseed oil. The oil, after 43 hours heating, may be said to be approximately in the condition of the boiled oil film of the preceding table about 3 hours old.

Stand Oil.—Sp. gr. $\frac{15.5}{15} = 0.972$ (results, this laboratory).

Bromine addition figure $\frac{51.6}{7.2}$ } McIlhiney method.
"substitution"

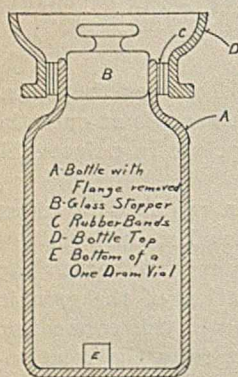


FIG. B

BROMINE ABSORPTION APPARATUS

Insoluble hexabromides none—Hehner and Mitchell method.

In connection with the method of Dr. McIlhiney, I have devised a convenient form of small funnel which can be constructed by any experimenter and will make the running in of the KI solution much more handy (see Fig. B).

The small cup cut from the bottom of 4 cc. homeopathic vial serves also in weighing out acetone for its determination by the Sy iodoform volumetric method.

Allen, 3rd edition, Vol. II, Part I, p. 66, gives:

Consistency*	Iodine value
Thin.....	163 to 175
Stout.....	99.5
Very stout.....	96.9

*Boiled Linseed oils.

The Stand Oil mentioned above was of a molasses consistency. Allen's very stout oil must approach the consistency of a medium printers' varnish.

If we can succeed in establishing the conditions under which a linseed oil film will dry in a normal manner we shall have a quantitative method at our disposal.

Albert H. Hooker had worked out a practical process for testing drying oils and driers earlier than 1904 on the basis of Weger's results. The form of apparatus in use by A. H. Hooker consisted of a 3 inch glass crystallizing dish, a small pestle or tamper made by melting the end of a glass rod and upsetting the same, and about 10 grams of finely ground natural silica. One gram of oil or of oil and drier mixture is used in each case and thoroughly incorporated with silica, weighings being taken every 5 minutes at the start until the minimum weight is attained and as often thereafter as may be necessary to obtain an accurate and smooth curve. Often two tests are started on the same day, one at about 8 A.M. and one at about 4 P.M. so as to get complete curves as in the case of the ordinary and double boiled oils.

Lippert calls attention to the importance of detecting the time and amount of the maximum gain in weight, a point not fully appreciated by the above mentioned sub-committee when working with boiled linseed oil. (The practical painter expects to get a boiled oil which will dry in a thin film on glass at 20° C. in less than 24 hours, and if additional driers were added to such an oil the experimenter would have to look for the maximum point before breakfast if the test were started on the day previous.)

The above process of mixing silica and oil is rather tedious and I have expedited the process by using ethyl ether as a vehicle. A tinned-iron can cover about 2 1/2 inches in diameter with a 1/4 inch rim is used as the weighing vessel. One gram of oil is weighed into it and about 10 grams of silica dropped on the oil. By the aid of a spatula and 3 to 5 cubic centimeters of ether the oil and silica are transferred to a large clock glass and then, after thorough mixing, returned to the can cover and the proper weighings made as indicated above.

Liverseege and Elsdon¹ give comparisons of iodine values with percentage gains in drying on powdered

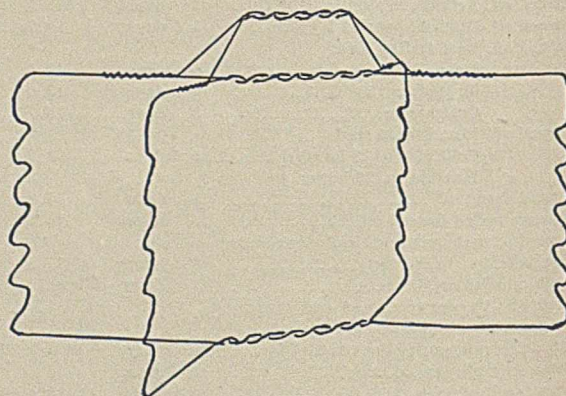


FIG. C—ALUMINUM WIRE PLATE HOLDER FOR HOLDING FIVE ALUMINUM PLATES, EACH 3 IN. X 6 IN., GIVING A TOTAL OF 180 SQ. IN., OF SURFACE

litharge for 8 raw oils and 5 boiled oils. They use a metal container and methylated ether.

¹ *J. Soc. Chem Ind.*, Mar. 15, 1912.

Lippert¹ used aluminum plates for a while but had no good way of cleaning them and abandoned their use in favor of glass apparatus. Since a dried linseed oil film is readily softened by means of 2 to 3 alcohol to benzole mixture, the aluminum is the proper basis for applying a drying test.

The Standard Varnish Works of Chicago were using a convenient form of apparatus in the latter part of 1904. This apparatus consisted of 5 aluminum plates each 3 inches by 6 inches, and therefore showing a total of 180 square inches of surface. These five plates are held by an aluminum wire frame at intervals of about $\frac{3}{8}$ inch (see Fig. C).

The complete apparatus weighs less than 80 grams and is conveniently weighed on the ordinary analytical balance. The quantity of non-volatile liquid to be applied is kept between 0.500 and 0.700 gram. It is usually applied at the rate of about 2 drops per surface, being uniformly distributed with the tip of a finger. The apparatus is hung under an open shelf to prevent the accumulation of dust. Weighings are made just as in the test on silica.

Results obtained with both forms of apparatus check nicely, as take the case of a bleached oil recently examined:

Specific gravity by Westphal balance $\frac{15.5^\circ}{15}$ equals 0.933.

Acidity as oleic acid equals 6.22 per cent.

The writer has used these forms of apparatus successfully for eight and seven years, respectively, and finds the oxygen absorption test to be quite as reliable a test as any other single test.

The addition of a drier hastens the drying but also reduces the actual proportion of drying oil present and in addition decreases the gain in weight of

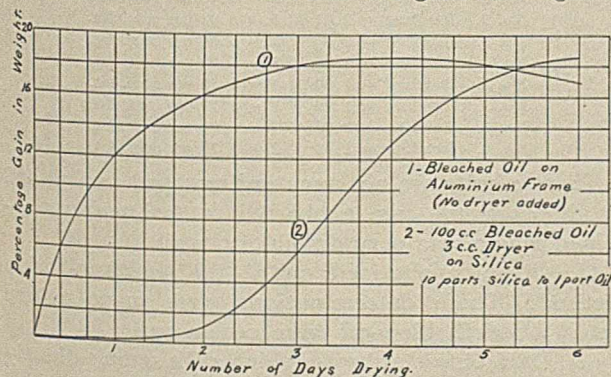


FIG. D

that drying oil which is present.

The addition of a drier is equivalent to a rise in temperature. As oxidation increases the viscosity of linseed oil, I have no doubt that some day specifications for boiled linseed oil will include data on viscosity along with data on the gain in weight.

In conclusion, it may be well to call attention to the fact that tests should be made only:

a. Along with a control oil of known purity or character.

- b. Using uniform amounts of drier.
- c. Using uniform temperature.
- d. Using definite limited thickness of film.
- e. In an atmosphere of moderate humidity.
- f. With free access of air.
- g. Under the same degree of illumination.

For the convenience of those readers who have not the time to study out the meanings of the technical expressions occurring in the German trade journals, the following translations are given:

<i>Firniss</i> ,	Boiled oil.
<i>Leinoelfirniss</i> ,	Boiled linseed oil.
<i>Lack</i> ,	Varnish.
<i>Lackfarbe</i> ,	Lake Color, Lake.

The author would call attention to the new work, "Die Chemie der Trocknenden Oele," by Wilhelm Fahrion, published by Julius Springer, Berlin, which also makes some references to the results of the work of the linseed oil sub-committee of the American Society for Testing Materials.

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CHICAGO

A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING MILK-FAT IN EVAPORATED MILK AND MILK POWDERS

By E. P. HARDING AND GUY PARKIN

Received Aug. 12, 1912

The methods in use at the present time for determining milk-fat in evaporated milk and milk powders are inadequate for the use of the manufacturer of these products, either giving too low results or requiring so much time as to make them impracticable. When the percentage of fat in these products becomes a matter of federal state and municipal control, it is necessary that methods be used in their analysis which will record all the fat in order that due justice be given the manufacturer and that they be sufficiently rapid to permit their use in control work.

It is well known that the original Babcock centrifugal method, which is the most rapid of all volumetric methods for determining fat in normal milk, gives by far too low results on the condensed product. Various modifications of this method which have been suggested as giving reliable results were tried out and all found to give too low results, special emphasis having been given to A. E. Leach's modification,¹ and the modification of O. F. Hunziker and G. W. Spitzer.² These methods give not only too low results but also an impure fat and a fat column very difficult to read.

Of all gravimetric methods in use, the Werner-Schmidt method and the Roese-Gottlieb method³ give the most reliable results. The former method almost invariably gives an impure fat which must be purified by dissolving the dried fat in petroleum ether and filtering. The latter method gives a pure fat but does not remove it all. Results obtained by this method and Hortvet's modification of the same (modified by using a smaller amount of milk in the process) follow later in this paper.

¹ *Analyst*, 25, 317.

² *Bull.* 134, Purdue Univ. Agric. Experiment Station.

³ *Circ.* 66, Dept. of Agr.

¹ *Chem. Rev. Fett. Harz Ind.*, 1897, 325.

The direct extraction methods like Adams' Paper Coil method and its modifications¹ are impracticable, being too long and giving either too low results or an impure fat.

The writers of this paper, believing the direct extraction methods to be impracticable and the precipitation methods not sufficiently accurate, attempted to solve the problem by indirect extraction methods, *i. e.*, by first dissolving all protein and then extracting the pure fat by some suitable solvent or solvents, as is done in the Werner-Schmidt and Roese-Gottlieb methods. A modification of a method used by one of the writers and Lillian Nye for determining fat in cereals² was found to give excellent results both in amount and purity of fat.

The principle of the method is the breaking down of the emulsion by dissolving all protein in acetic acid, the solution of the fat in a mixture of alcohol and carbon tetrachloride and its extraction with petroleum ether.

The reagents used are acetic acid, 25 per cent. by volume, redistilled carbon tetrachloride, 95 per cent. ethyl alcohol and petroleum ether with boiling point between 50° and 70° C.

The apparatus used are a mortar and pestle for macerating the can's contents, an evaporating dish of about 50 cc. capacity for weighing out the sample, a 100 cc. flask for making up the 40 per cent. emulsion, a 10 cc. graduated pipette, a 100 cc. Nessler jar fitted with two rubber stoppers, one unperforated and used while centrifuging, the other doubly perforated, bearing blow-off tubes similar to the Werner-Schmidt blow-off tube, a centrifuge, a seven cm. filter paper, funnel and stand, wide-mouthed flasks of 50 to 75 cc. capacity for weighing the fat, a small evaporating dish for holding wash petroleum, a petroleum ether wash bottle, a condenser and drying oven.

In carrying out the process, the can's contents are placed in the mortar and macerated until thoroughly mixed. Forty grams of this mixture are weighed out in the dish, transferred to the 100 cc. flask, the dish well washed with water, the flask filled to the 100 cc. mark with water and then thoroughly shaken to insure a uniform mixture. Four cc. of this mixture are pipetted into the Nessler extraction jar or enough is accurately weighed in the jar to approximate 1.6 grams of the original sample, 8 cc. of acetic acid added and the contents warmed to about 50° C. by cautiously rotating the jar over a low flame or holding it in water of that temperature. When the protein has dissolved, 12.5 cc. of carbon tetrachloride are added and the jar vigorously shaken for two minutes, then 25 cc. of alcohol are added and the whole mixed by thoroughly shaking; 25 cc. of petroleum ether is then added and the jar vigorously shaken for two minutes, then 15 cc. more of the ether added and the shaking continued one minute longer. The jar is then corked and centrifuged for two minutes at the rate of about 70 revolutions per minute. The blow-off tube is then inserted and the ether layer cautiously blown onto the

filter, filtering it into the tared weighing flask. (In blowing off the ether layer, care must be taken that none of the carbon tetrachloride layer is blown off, which may happen if a too close separation of the two layers is attempted. This may be avoided by blowing slowly and observing if any bubbles rise in the tube. If bubbles are seen rising, the blowing is quickly discontinued and they are removed by gently sucking on the blow-off tube.) Five cc. of petroleum ether are then placed in the small evaporating dish and gently drawn into the jar by sucking on the blow-off tube. After a few moments this ether, which has mixed with the thin ether layer in the jar, is blown off and filtered as before. Five cc. of carbon tetrachloride are then added to the contents of the jar, which is thoroughly shaken, then 30 cc. of petroleum ether are added and the jar again thoroughly shaken, then centrifuged for one minute and the ether layer separated and washed once as in the first blow-off. Another addition of 5 cc. carbon tetrachloride and 30 cc. of petroleum ether is made and the separation of the ether layer repeated as in the first blow-off. The filter paper is then well washed with small portions of the petroleum ether, the flask connected with a condenser, the ether distilled off and the flask heated for an hour in an oven at a temperature of 100° C. and then weighed. A fourth blow-off is not necessary as is shown later in the paper.

During the process, while the jar is being prepared for the second and third blow-offs, the weighing flask is connected with the condenser and most of the ether distilled off. This shortens the process some and permits the use of a 50 to 75 cc. flask for weighing the fat.

I. Data obtained on Van Camp's Evaporated Milk by Hunziker's and Spitzer's Modification of Babcock's Method:†

No. 1.	Reading = 2.05 × 3 = 6.15 per cent. fat.
No. 2.	Reading = 2.01 × 3 = 6.03 per cent. fat.
No. 3.	Reading = 2.00 × 3 = 6.00 per cent. fat.
No. 4.	Reading = 2.00 × 3 = 6.00 per cent. fat.
No. 5.	Reading = 1.90 × 3 = 5.70 per cent. fat.
No. 7.	Reading = 1.90 × 3 = 5.70 per cent. fat.
No. 8.	Reading = 2.00 × 3 = 6.00 per cent. fat.
No. 9.	Reading = 1.90 × 3 = 5.70 per cent. fat.

These results are not very uniform and are low and in almost every case a charred fat column was obtained which was very difficult to read.

II.—Results obtained with the Harding-Parkin Method: These determinations were made to find out if a fourth blow-off were necessary.

(a) Data obtained by weighing milk sample directly from can without solution. Van Camp's brand of milk was used and each determination represents a different can sample.

No.	1st and 2nd blow-offs		3rd blow-off		4th blow-off	
	Gram	Percent- age	Gram	Percent- age	Gram	Percent- age
1	0.1252	8.25	0.0002	0.01	0.0002	0.01
2	0.1285	8.67	0.0006	0.04	0.0004	0.02
3	0.1366	8.26	0.0004	0.02	0.0003	0.01
4	0.1224	8.12	0.0020	0.10	0.0000	0.00
5	0.1226	8.30	0.0016	0.10	0.0001	0.00
6	0.1456	8.20	0.0020	0.11	0.0002	0.01
7	0.1263	8.25	0.0016	0.10	0.0000	0.00

¹ *Analyst*, 30, 128. *Bull.* 134, Purdue Univ. Agric. Experiment Station.

² *This Journal*, 4, 895.

[†] *Bull.* 134, Purdue Univ. Agric. Experiment Station.

(b) Data obtained by using a 40 per cent. emulsion of the milk:

No.	1st and 2nd blow-offs		3rd blow-off		4th blow-off	
	Gram	Percent-age	Gram	Percent-age	Gram	Percent-age
1	0.1295	8.33	0.0005	0.03	0.0003	0.02
2	0.1182	8.34	0.0005	0.03	0.0003	0.02
3	0.1279	8.67			0.0001	0.00

It will be observed that by comparing the data in (a) and (b) that a fourth blow-off is unnecessary and that no error arises in using a 40 per cent. emulsion. There is also less chance of error in sampling in using a 40 per cent. emulsion.

III. (a) A comparison of data obtained on different brands of milk by the Harding-Parkin Method and the Roese-Gottlieb method as given in *Circ. 66*, Dept. of Agric. These results were determined on samples weighed instead of measured and each determination represents a different can of milk. The starred determinations were run on a 40 per cent. emulsion and the rest on the sample directly from the can:

VAN CAMP'S BRAND

No.	Harding-Parkin Method			Roese-Gottlieb Method			Diff. Per cent.
	Milk Grams	Fat Gram	Fat Per cent.	Milk Grams	Fat Gram	Fat Per cent.	
1	1.5100	0.1325	8.77	4.0444	0.3296	8.14	0.63
2	1.0436	0.0893	8.55
3	1.5177	0.1252	8.25	4.1270	0.3252	7.87	0.38
4	1.5069	0.1244	8.22	4.0542	0.3250	8.01	0.12
5	1.5292	0.1263	8.25
6	1.4764	0.1242	8.40	3.9948	0.3175	7.96	0.44
7	1.7786	0.1476	8.31	4.0466	0.3270	8.08	0.23
8	3.8191	0.1295	8.33	10.2476	0.3282	7.87	0.46
9	3.4816	0.1182	8.34	10.0283	0.3135	7.70	0.64
10	4.8942	0.1622	8.21	10.8776	0.3485	7.87	0.34

(b) The following data were obtained on a 40 per cent. emulsion. The first three determinations were run on the same can sample and 4 cc. were used in the Harding-Parkin method, representing 1.6 grams of the original sample and 10 cc. in the Roese-Gottlieb method representing 4 grams of the original sample:

ANALYSIS OF A 40 PER CENT. EMULSION

Brand	Harding-Parkin			Roese-Gottlieb			Diff. Percent-age
	Milk Grams	Fat Gram	Fat Percent-age	Milk Grams	Fat Gram	Fat Percent-age	
Pet.....	1.60	0.1735	10.84	4	0.4088	10.22	0.62
.....	1.60	0.1731	10.81	4	0.4143	10.37	0.44
.....	1.60	0.1730	10.81	4	0.4091	10.22	0.59
.....	1.60	0.1308	8.16	4	0.3020	7.55	0.61
.....	1.60	0.1415	8.84	4	0.3281	8.20	0.64
.....	1.60	0.1368	8.55	4	0.3276	8.19	0.36
.....	1.60	0.1346	8.41	4	0.3248	8.12	0.29
.....	1.60	0.1302	8.13	4	0.3080	7.70	0.43
.....	1.60	0.1368	8.55	4	0.3250	8.12	0.43
Peerless... 1.60	0.1254	7.84	4	0.3020	7.55	0.29	
... 1.60	0.1268	7.92	4	0.3010	7.52	0.40	
... 1.60	0.1242	7.76	4	0.3016	7.54	0.22	
... 1.60	0.1245	7.78	4	0.3002	7.50	0.28	

IV. The results in IV were obtained on a 40 per cent. emulsion, the amount of milk used being meas-

ured as in II(b). The method used for comparison was a modification of the Roese-Gottlieb method by Hortvet, one-half as much sample being used as in the Roese-Gottlieb method and one additional blow-off being made. Each determination represents a different can sample:

ANALYSES OF A 40 PER CENT. EMULSION

Brand	Harding-Parkin			Hortvet modified Roese-Gottlieb			Diff. Per cent.
	Milk Grams	Fat Gram	Fat Per cent.	Milk Grams	Fat Gram	Fat Per cent.	
Dundee.....	1.6	0.1297	8.11	4	0.1454	7.27	0.84
Tacco.....	1.6	0.1286	8.04	4	0.1512	7.56	0.48
".....	1.6	0.1240	7.75
Meadow.....	1.6	0.1261	7.88	4	0.1566	7.83	0.05
".....	1.6	0.1174	7.34	4	0.1530	7.15	0.19
Dakonun.....	4	0.1454	7.27
".....	1.6	0.1200	7.50	4	0.1460	7.30	0.20
Batavia.....	1.6	0.1395	8.72	4	0.1562	7.81	0.09
Poppy.....	1.6	0.1603	10.02	4	0.1882	9.41	0.61
Princess.....	4	0.1540	7.70
Cornell.....	1.6	0.1363	8.52	4	0.1634	8.17	0.35
Kahaka.....	1.6	0.1392	8.70	4	0.1610	8.05	0.65
Van Camp.....	1.6	0.1289	8.06	4	0.1554	7.77	0.29
Beauty.....	1.6	0.1328	8.30	4	0.1632	8.16	0.14
University.....	1.6	0.1279	7.99	4	0.1566	7.83	0.16
Cottage.....	1.6	0.1344	8.40	4	0.1658	8.29	0.11
Breakfast.....	1.6	0.1350	8.44	4	0.1684	8.42	0.02
Yours Truly....	1.6	0.1501	9.38	4	0.1862	9.31	0.07
Columbian.....	1.6	0.1221	7.63	4	0.1506	7.53	0.10
Botavia.....	1.6
Every Day.....	1.6	0.1222	7.64
Monarch.....	1.6	0.1291	8.07
Gold Cross.....	1.6	0.1253	7.83	4	0.1544	7.72	0.11
Peerless.....	1.6	0.1163	7.17	4	0.1428	7.14	0.13

The determinations in IV were made by Mr. Parkin in Mr. Hortvet's laboratory with the purpose of checking the two methods. The results agree quite closely and, with the exception of three determinations, give an average difference of 0.166 per cent. in favor of the Harding-Parkin method.

To determine whether all the milk fat was removed by the petroleum ether from the admixture of water, alcohol and carbon tetrachloride, a sample of butter fat was purified and dried to constant weight and then put in a solution in the carbon tetrachloride and treated similarly to the milk emulsion.

0.1170 gram of butter fat was taken and 0.1169 gram recovered, giving a recovery of 99.90 per cent.

In conclusion, the writer feels justified in recommending this method for use in the analysis of desiccated milk for the following reasons:

1. It is a short practical method readily adapted to commercial work.
2. It gives a pure fat.
3. It gives a higher per cent. of pure fat than other methods in use.
4. It will give accurate results without a close adherence to the amounts of reagents specified.
5. Justice will be done the desiccated milk manufacturer.

It has been found by a large number of determinations made since the above data were obtained that the use of a centrifuge is not necessary and instead of centrifuging as given in the method after adding the petroleum ether and shaking, the jar is allowed to stand for two minutes, when the separation of the

two layers is complete. In a few cases an emulsion was formed which was immediately broken by adding a few drops of alcohol. The writers therefore make this change in the method, as previously described.

The new method gives good results on chocolate ice cream, where other methods on account of the chocolate fiber have failed to give reliable and accurate results. In applying the method to ice cream, a representative sample was melted, well mixed and 5 grams taken for analysis, 5 cc. of acetic acid, 12 cc. of carbon tetrachloride, 20 cc. of alcohol and 30 cc. of petroleum ether were added and the process carried out as with condensed milk.

The following data were obtained with this method and two other methods on three samples of ice cream, each determination representing a different sample:

Weight taken	ANALYSES OF ICE CREAM Harding-Parkin		West ¹ Percentages of fat	Modified Babcock ²
	Fat, Gram			
5 grams.....	0.6603	13.20	11.75	12.00
5 grams.....	0.6050	12.10	10.00	11.00
5 grams.....	0.8152	16.30	15.00	15.50
5 grams.....	0.6579	13.15	12.00	12.50

¹ West's method is described in the Twelfth Biennial Report of the Minnesota State Dairy and Food Commissioner, p. 56.

² The Modified Babcock Method is described in Food Inspection and Analysis by Leach, 1909 Edition, p. 200, under the heading "Second Method," and a reference is given to Rep. Illinois State Food Commissioner, 1909, p. 80.

The method is at present being tried out on various ice creams, on cheese, cereals, flours and various other products.

Since this paper was written, a modification of Babcock's Volumetric Method by W. Gregory Redmond has appeared in the July, 1912, number of THIS JOURNAL.

UNIVERSITY OF MINNESOTA
MINNEAPOLIS

THE RATE OF THE REACTION OF NITROUS ACID AND UREA IN DILUTE SOLUTIONS

By W. D. BONNER AND E. S. BISHOP

Received Sept. 20, 1912

In Notice of Judgment No. 722, Food and Drugs Act, the following statement¹ is made by Dr. W. S. Haines, a witness for the appellant:

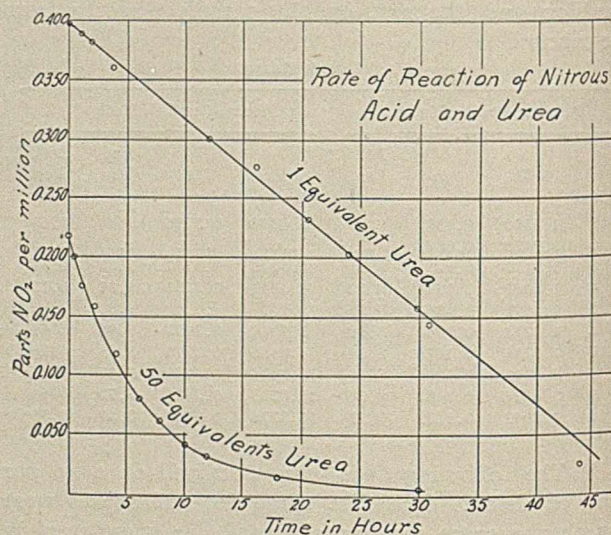
"I believe when nitrites are taken into the body by the mouth that, as they pass into the stomach and the material becomes acid, there are certain substances present in the stomach which cause their decomposition; among others, urea, which is found in the saliva. Urea, it is well known, in the presence of an acid and a nitrite, decomposes the nitrous acid of the nitrite—liberating nitrogen, water and carbonic acid gas. I believe that nitrites, taken into the stomach with our food, are very largely, if not completely, decomposed in the stomach in this way. At body temperature, urea and nitrites react within half an hour."

In the same publication, Dr. S. F. Acree, a witness for the libellant, is reported as saying that he had made experiments to determine whether or not nitrous acid and urea react at body temperature and had found that a solution containing 0.1 part of nitrite nitrogen per million, the average amount assumed

to be present in human saliva, with the equivalent amount of urea and 0.2 per cent. HCl, did not react appreciably in 2 hours, nor was there any appreciable reaction in that time when the concentration of urea was increased 50-fold.¹ He also testified that solutions of the above concentrations do not react appreciably in 17 hours.²

Some experiments performed by one of us during the course of this trial, as well as theoretical considerations, led us to believe the results of this latter witness, and perhaps of both of them, to be in error. They also seemed to indicate that the certainty of the reaction might depend on the purity of the urea used. The following embodies the results of our experiments to settle these two points.

With regard to the second point, we have tried all the samples of urea in the laboratory, including samples of all grades of purity, and have found them, every one, to react with a given sample of nitrous acid, *i. e.*, with a nitrite in acid solution. We have also tried all the nitrites at our disposal, of which there were several samples each of sodium, potassium and



ammonium nitrites, and have found that all of them react readily with urea. The reaction takes place in acid solution only, never in neutral or in alkaline solutions. We do find, however, that sometimes, when working with dilute solutions, one of a pair of duplicates reacts normally, while one does not react. We have not found this behavior in the case of solutions of a concentration as great as 1 part of NO₂ per liter, but when the concentration is 0.1 part per million the occurrence is too frequent to be a mere accident. We have no explanation to offer, but the matter will be investigated further.

As for the other point, *viz.*, the rate of the reaction, reference to the curves will show that both the gentlemen cited above were very decidedly in error.

EXPERIMENTAL

The sodium nitrite and the urea used in these experiments were Kahlbaum's best reagents, and the laboratory distilled water was quite free from ni-

¹ Notice of Judgment, No. 722, page 100.

² Transcript of Record, No. 3543, page 1956.

¹ Notice of Judgment, No. 722, p. 97.

trites. Two methods of preparing the reaction mixture were used. The one was to pipette out separately, from stock solutions of suitable strength, the sodium nitrite and the urea, and to add to the resulting solution sufficient HCl to make the whole 0.3 per cent. HCl. The other was to prepare a stock solution containing both the sodium nitrite and the urea in the desired concentrations, run this into the reaction flasks from a burette, and to add the HCl also from a burette. The latter method was the more satisfactory, since the relation of sodium nitrite to urea was thus always the same, and the actual concentration varied only as the amount of added HCl varied. By adding the acid from a burette this variation could, with reasonable care, be made quite negligible. Before adding the acid the flasks containing the reaction solution were placed in the constant temperature bath and allowed to come to the bath temperature, 37.5°. The bath was electrically heated and controlled and was constant to $\pm 0.1^\circ$. When the reaction solution had come to the temperature of the bath the acid was run in, and the solution then stood in the bath, portions being withdrawn at suitable intervals for the purpose of determining the amount of nitrous acid remaining, until the reaction was complete, or until the solution was exhausted. The nitrous acid was determined by means of the well known Griess-Ilosvay reaction,¹ the color being allowed to fully develop and then compared, in a Schreiner colorimeter, with a standard of known nitrous acid content. The time necessary for the full development of the color we found to be considerably greater than usually stated in the text-books. Sutton says:²

"The solutions are allowed to stand 15 minutes before the pink colors are compared." We find, however, that except in cases where the concentration of NO_2 is greater than 1 part per million the solution should stand a half hour, and when the concentration is very small, 1 or even 2 hours will be needed.

DISCUSSION

That urea and nitrous acid in equivalent quantities should not react to an appreciable extent in 2 hours is perhaps not surprising when one considers the extreme dilution of the solutions, 0.1 part of nitrite nitrogen, or 0.33 part of NO_2 , per million. But when one considers the delicacy of the Griess reaction, detecting easily 1 part of NO_2 per 200 million,³ it seems strange that the progress of the reaction could not be detected in 17 hours. When, however, the concentration of urea was increased to 50 equivalents it would be very strange indeed if the rate of the reaction were then not appreciable. An interesting explanation of how such results as these were got is had by consulting the transcript of record of this case.⁴

There Dr. Acree states that, having mixed the nitrite and the urea solutions and having added the HCl and the Griess reagent, if the nitrous acid and the

urea then react the color of the solution will become lighter, and if the reaction becomes complete the solution will become colorless, "transparent in color." That such is not the case may be seen from the following *a priori* consideration.

Urea and nitrous acid react to produce nitrogen, carbon dioxide and water. Nitrous acid and sulphanilic acid react to produce a diazo compound, which in turn reacts with the α -naphthylamine to produce the dye which is characteristic of the Griess-Ilosvay reaction.¹ Of these two reactions the latter has much the greater rate, *i. e.*, a given amount of nitrous acid will be decomposed by the Griess reagent in much less time than the same amount of nitrous acid would be decomposed by urea. Proof of this is seen in the fact that the one reaction can be used for the detection and estimation of nitrous acid in the presence of urea, that is, while the other reaction is actually in progress. Since the two reactions are simultaneous the situation is analogous to that of two bases competing for less than a sufficient amount of an acid. In this case the "ratio of distribution is equal to the ratio of the respective degrees of dissociation," *i. e.*, the ratio of distribution² is equal to the ratio of the speeds with which the two bases react with one and the same acid. In the present case we have two simultaneous reactions, one of which, when using 50 equivalents of urea, is completed in approximately 24 hours, the other in a half hour or less. When equilibrium is reached, therefore, not more than $1/48$ of the nitrous acid will have reacted with the urea, the rest with the Griess reagent, and no further reaction will occur. Starting with a concentration of nitrous acid of 0.1 part of nitrite nitrogen per million, the difference in color produced by $1/48$ of the nitrous acid reacting with the urea would not be appreciable, the solution could not be distinguished by color from one of the same concentration of nitrous acid and containing no urea. To show that this is actually the case, and that the solution will not become colorless on standing after the Griess reagent has been added, we prepared solutions containing 0.2 part of nitrite nitrogen per million, 1000 parts of urea per million, HCl to make 0.3 per cent. solution, and added the Griess reagent at once. Blanks containing the same concentration of nitrous acid, but no urea or HCl, were prepared, and also duplicates to which the Griess reagent was not added at once, but in which the course of the reaction was followed in the usual manner. These duplicates showed the reaction to be complete in one hour. At the end of 5 hours the solutions containing the Griess reagent were little if any lighter in color than the blanks which contained no urea, and after standing at 37.5° for more than a month the colors were not perceptibly different.

RÉSUMÉ

It has been shown:

(1) That nitrous acid and urea react at an appre-

¹ The Griess-Ilosvay reagent is sulphanilic acid and α -naphthylamine dissolved in acetic acid. For the course of this reaction see Griess, *Ber. d. chem. Ges.*, 427, 1879.

² Nernst, "Theoretische Chemie," 5 Auflage, s. 516.

¹ Sutton, "Volumetric Analysis," 9th Edition, p. 449.

² *Ibid.*, p. 449.

³ See Warrington, *Jour. Chem. Soc.*, 232, 1881.

⁴ Transcript of Record, No. 3534, page 1956.

ciable rate even when the initial concentrations are so low as 0.1 part of nitrite nitrogen per million, and urea in equivalent amount.

(2) That once having added the Griess reagent, and thus converted the nitrous acid into the characteristic dye, urea will not then react with the nitrous acid, even though present in great excess.

(3) That nitrous acid and urea, in very dilute solutions, sometimes fail to react, for no apparent reason.

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THE INFLUENCE OF A PRECEDING CROP ON NITRIFICATION IN SOIL

By T. LITTLETON LYON AND JAMES A. BIZZELL

Received Sept. 11, 1912

While the practices of crop rotations have been fairly well worked out there yet remains much to learn regarding the underlying principles. Most of the effort in experimentation with soils has been to ascertain the effect of certain soil conditions on plant growth or on the solubility of the mineral nutrients in various solvents. The study of the principles of crop rotation will necessitate the investigation of the effect of plant growth on the soil. The fact that a certain plant grows better when preceded by one species of plant than by another is a self-evident indication that plants of different species exert different influences on the soil.

The writers have suggested¹ that certain higher plants have a distinct influence on the process of nitrification in the soil; that this influence varies in intensity with plants of different families, and at different stages in the growth of any one kind of plant. It was found, for instance, that in a soil on which maize was growing the nitrates were sometimes higher at certain periods than in a similar soil on which no plants grew. Timothy (*Phleum pratense*), on the other hand, maintained uniformly a very low nitrate content in the soil throughout the growing period.

The question then arose whether the higher plants exerted any influence on the activities of the nitrifying bacteria after the plants had been removed. To test this it was decided to continue the nitrate determinations a second year in soil that had been planted to several kinds of crops.

Plats that were used for studying the effect of plants on the nitrate content of soils in 1910 were kept bare in 1911 until July 1st. To keep down the weeds the plats were disc harrowed from time to time. Samples of soil were taken from the sections of the plats that were planted and bare in 1910, in order to ascertain the effect of the different crops grown the previous year on the nitrate content of the soil. Soil samples were taken from both the previously planted and unplanted sections of the plats, and the borings were made to a depth of eight inches from the surface, and again from eight to sixteen inches. Table I presents the results, averaged for the entire season, for the four plats planted to the same crop, also the average of the unplanted sections of the same plats during the

growing season of 1910, and consequently shows the nitrate content of the soil in the year during which the test crops were grown:

TABLE I—NITRATES IN PLANTED AND UNPLANTED SECTIONS OF PLATS AVERAGE FOR THE GROWING SEASON

Plat Nos.	Crop	On basis of		Nitrogen in crop Lbs. per acre
		Nitrates p. p. m. dry soil	nitrates in bare soil 100	
3612, 13, 22, 23.....	{ Maize	167	123	3.5
	{ None	136	100	
3614, 15, 24, 25.....	{ Potatoes	104	96	42.7
	{ None.	108	100	
3616, 17, 26, 27.....	{ Oats	90	71	28.7
	{ None	126	100	

The nitrates were highest under the maize, next highest under the potatoes and lowest under the oats. Similar results had been obtained in previous years.

The last column of Table I shows the quantity of nitrogen removed per acre by each crop. The maize crop was a very poor one, which accounts for the small quantity of nitrogen contained in that crop. It is doubtless true that the small maize crop is partially responsible for the high nitrate content of the maize soil, but this high nitrate content has been found in maize soil in previous years when the crop was good. Again, the persistently higher nitrate content of the maize soil, as compared with the bare soil, can be explained only on the assumption that nitrification is much more active where the maize is growing, for certainly more nitrates are being removed from the planted soil.

Nitrates are higher in the potato soil than in the oat soil, although the former crop removed fifty per cent. more nitrogen. The nitrate content of a planted soil is not determined by the total quantity of nitrogen removed by the crop, but by a number of factors, of which one appears to be a direct influence which each species of plant exerts on the activity of the nitrifying organisms.

The year following that in which the results given above were obtained these plats were kept free from vegetation until July 1st and nitrates were determined from time to time. Table II contains a statement of the nitrates of the previously planted and bare sections of these plats on each of the dates when the soils were analyzed:

TABLE II—NITRATES IN SOIL PLANTED THE PREVIOUS YEAR AND SOIL UNPLANTED

Plat Nos.	Crop.	May 1		June 5		June 28	
		First	Second	First	Second	First	Sec'd.
		8 in.	8 in.	8 in.	8 in.	8 in.	8 in.
3612, 13, 22, 23...	{ Maize	51.5	53.4	77.9	44.6	40.5	34.0
	{ None	48.1	52.3	68.0	44.0	40.3	30.1
3414, 15, 24, 25...	{ Potatoes	31.3	26.0	49.8	26.4	28.6	23.9
	{ None	42.7	43.0	79.7	42.6	35.2	29.4
3616, 17, 26, 27...	{ Oats	22.7	20.7	41.1	33.0	22.1	21.6
	{ None	32.3	39.6	68.4	34.8	33.6	31.9

An examination of this table will show that, except in the case of maize, the nitrates are lower in the soil on which plants grew the previous year than in the soil kept bare at that time. It will also be noticed that the nitrates on this bare soil are in the same order as they were when the plats were planted. That nitrates are highest in the soil previously planted to

¹ Journal of the Franklin Institute, Jan. and Feb., 1911, pp. 1-16, 205-220.

maize, next in that planted to potatoes, and lowest in that planted to oats.

In Table III is given a statement of the nitrates in the planted sections of the plats in terms of the nitrates in the unplanted sections taken as 100. To obtain this the nitrates in both planted ends of the four plats planted to the same crop are averaged and this is divided by the average for the nitrates on the unplanted sections of the corresponding plats. This furnishes the most accurate means of comparison as it removes more effectively than any other method the local variations in the nitrate content of the soil.

TABLE III—RATIO OF NITRATES IN BARE SOIL TO NITRATES IN SOIL OF SAME PLATS PREVIOUSLY PLANTED.

Plat Nos.	Crop.	Surface 8 inches.			Second 8 inches.		
		May	June	June	May	June	June
		1	5	28	1	5	28
3612, 13, 22, 23...	Maize	108	114	100	102	101	112
3614, 15, 24, 25...	Potatoes	73	63	81	60	62	81
3616, 17, 26, 27...	Oats	70	60	66	53	95	68

There is a distinct and characteristic difference in the nitrate content of the soil previously bearing these different plants. While the experiment covers only one season the differences would seem to be too large and well defined to be accidental.

Maize is the only crop following which the nitrates in the planted soil are higher than in the unplanted soil.

These results serve to support the idea already advanced by the writers, that higher plants influence the nitrifying process in soils.

On July 1st the plats used in this experiment were drilled to millet, the entire plat being planted, including the middle section of each plat, which during the preceding year had remained bare. The object in planting the millet was to see how the growth of a crop of these plats would correspond with the nitrate content.

On September 8th careful notes were taken of the growth on each plat and a comparison made not only between different plats but also between the growth of the millet on the previously planted section and the bare section of each plat.

The growth of millet was in each plat markedly better on the sections of the plat that had been in crop the previous year than on the unplanted section. This applied to every crop in the experiment. A comparison of the growth on the planted sections of the plats is given in Table IV, in which the growth of millet on the plats planted to oats is taken as 100 and the growth on the other plats stated on this basis:

TABLE IV—GROWTH OF MILLET ON THE PLATS PLANTED TO DIFFERENT CROPS THE PREVIOUS YEAR

	Soil treatment	Plat No.	Growth of millet		Average growth of millet	
			Per cent.	Per cent.	Per cent.	Per cent.
Maize.....	No lime	3612	37	3622	62	49
	Lime	3613	47	3623	71	59
Potatoes....	No lime	3614	60	3624	81	70
	Lime	3615	65	3625	88	76
Oats.....	No lime	3616	100	3626	100	100
	Lime	3617	100	3627	100	100

It will be seen that the luxuriance of the growth of millet on these plats was inversely proportional to the relative concentration of the nitrates in the soil. For instance, the millet made the best growth on the plats planted to oats and these plats had the lowest nitrate content. The poorest growth of millet was on the maize plats and these had the highest concentration of nitrates.

In Table V the ratio of nitrates to bare soil of the surface eight inches of the several plats on June 28th, which was only a few days before the millet was planted, is compared with the percentage growth of millet on the same plats.

TABLE V—COMPARISON OF NITRATES IN SOIL PLANTED TO CERTAIN CROPS AND THE GROWTH OF MILLET ON THE SAME PLATS

Crop in 1910	Relative nitrate content	Relative growth of millet
Oats.....	59	100
Potatoes.....	67	73
Maize.....	100	54

It would seem from these results that, in this soil, the conditions that favored the growth of millet were unfavorable to the formation of nitrates. That this is not true of other conditions is evident from the fact that the millet grew better on the limed than on the unlimed soil, as shown in Table IV, while the nitrates are also higher in the limed plats, as may be observed in Table VI, which follows:

TABLE VI—NITRATES IN UNPLANTED SECTIONS OF PLATS LIMED AND NOT LIMED.

Plat Nos.	Soil treatment.	Nitrates in soil, p. p. m.			
		May 4	June 5	June 28	Avr.
{ 3612, 22.....	No lime	40.5	61.2	41.8	47.8
{ 3613, 23.....	Lime	54.8	74.9	38.7	56.1
{ 3614, 24.....	No lime	39.9	76.9	34.3	50.3
{ 3615, 25.....	Lime	45.4	82.5	36.0	55.0
{ 3616, 26.....	No lime	28.5	51.7	36.2	38.8
{ 3617, 27.....	Lime	36.2	85.2	40.3	53.9

It is quite evident that although the previous crop influences greatly the nitrate content of this soil, the growth of millet is not increased thereby. Nitrates are not the limiting factor in the growth of millet on this soil.

Lime increases the growth of millet and also the formation of nitrates, but apparently its beneficial action must be due to some cause other than its influence on nitrate formation.

The purpose of this paper is to call attention to the influence of certain kinds of plants on the formation of nitrates in the soil after the crops have been removed. The relation of the nitrate formation to the growth of millet on this soil is a separate problem, probably peculiar to this particular soil, but possibly worth recording in passing. The interesting condition exists that, of the crops used in the experiment, each had a certain and distinct influence on nitrate formation following the removal of the crops, and on the growth of millet also following their removal, but that the effectiveness of the influence is directly opposite. It is not to be expected, however, that this opposite effect would obtain in all soils, since the presence of an abundance of nitrates would, under some circumstances, throw the influence towards a better

growth of the succeeding crop. There is thus presented a problem in crop rotation. If the influence of a certain kind of plant on the formation of nitrates, after its removal, holds for soils, other than the one used in this experiment, something has been learned. That other, and under some conditions, influences more potent than nitrate formation obtain is also indicated by this experiment.

SUMMARY

Plats of land planted to certain crops in 1910 were kept bare of vegetation during the early part of the growing season of 1911. Determinations of nitrates, in the soil of these plats showed a distinct and characteristic relation of the several plants to the nitrate content of the soil in the year following that in which the plants were grown.

Maize was the only crop following which the nitrates in the previously planted soil were higher than in the unplanted soil. Potato soil was the next highest in nitrates, and oat soil contained least nitrates.

Millet planted on these plats July 1st was markedly influenced by previous crops, but the luxuriance of growth was inversely proportional to the nitrate content of the plats.

The beneficial influence of a crop on a succeeding one was not, in this case, to be attributed to the favorable influence exerted on nitrification, but this would doubtless differ with different soils, and if this effect of certain plants on nitrification in the following year should be of general application, the influence of a crop on nitrification may be an important factor in crop rotation.

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A COMPARISON OF SOME QUALITATIVE AND QUANTITATIVE METHODS FOR CARBONATES IN SOILS

By E. W. GAITHER

Received Aug. 28, 1912

In connection with certain chemical investigations of soils, which are being conducted in the laboratory of the Chemical Department of this Station, it was found necessary to determine the carbon dioxide existing as carbonates in the soils.

After making a number of determinations by the official method,¹ it was found that there was no correlation between the reaction of the soils with litmus paper or the Veitch qualitative test and the CO₂ obtained by this method.

If it were assumed that the CO₂ was derived from carbonates and it were calculated to CaCO₃, the average amount for acid surface soils would be 3244 pounds CaCO₃ per 2,000,000 pounds of soil and that for acid subsoils would be 1036 pounds per 2,000,000 pounds of soil, which would be a sufficient amount of this material present to render any of these soils alkaline or to indicate that there was a sufficient amount of this compound in all of these soils for all practical purposes. In many cases, where the soil reddened blue litmus, more CO₂ was obtained than from those which turned red litmus blue. These

variations led to the conclusion that this method was unreliable as a measure of soil carbonates.

While considering this point, attention was directed by Mr. J. W. Ames, Chief of the Department, to a method devised by the late F. S. Marr, Carnegie Research Scholar, Rothamsted, England, and published in the *Journal of Agricultural Science*, Vol. III, Part 2, pp. 155-160, for determining CO₂ as carbonates in soils, in which the soil was boiled with very dilute acid under reduced pressure. It is claimed that under these conditions no organic matter is decomposed and that the CO₂ obtained is derived from carbonates only.

Some of Marr's work was repeated and his results were confirmed.

He found that CO₂ was evolved from acid soils even when boiled with distilled water at 100° C. and that the amount was increased upon the addition of a mineral acid, while if boiled at 50° C. under reduced pressure with 2 cc. of conc. HCl per 100 cc. of water, the results were either negative or only a very small amount of CO₂ was evolved. These results were considered to be within the limits of experimental error.

The double titration method of Brown and Escomb with the Amos apparatus⁴ was used by Marr, while a slight modification of the same method and an apparatus designed by the writer² was used in this work.³

In checking Marr's work, four soils were chosen, one acid, the other three giving from slight to strong alkaline reactions to litmus and progressive amounts of CO₂ with weak acid under reduced pressure. Comparative results under different treatments follow.

TABLE I—PER CENT. OF CO₂ BY DIFFERENT METHODS OF TREATMENT

Lab. No.	Per cent. CO ₂ when boiled at 100° C. with distilled water 2½ hours	Per cent. CO ₂ when boiled at 50° C. under reduced pressure with distilled water 2½ hours	Per cent. CO ₂ when boiled at 50° C. for 30 minutes under reduced pressure with 2 cc. HCl per 100 cc. of H ₂ O for 30 mins.		Reaction of soil to litmus paper
			Per cent. CO ₂ when boiled at 100° C. with 20 cc. of 1-1 HCl and 80 cc. of H ₂ O for 30 mins.	Per cent. CO ₂ when boiled at 50° C. for 30 minutes under reduced pressure with 2 cc. HCl per 100 cc.	
4715	0.025	0.00	0.190	0.00	Acid
4722	0.010	0.00	0.205	0.01	Sl. alk.
4724	0.015	0.00	0.175	0.03	Alk.
4731	0.265	0.04	4.700	4.62	St. alk.

ABBREVIATIONS USED IN THE PRECEDING AND FOLLOWING TABLES.

A. = acid, Sl. = slightly, St. = strongly, Alk. = alkaline.
Mi. = Miami, V. = Volusia, D. = Dunkirk, Wab. = Wabash and B. or Blk. = Black, Gr. = Gravel, Sd. = Sand, Si. = Silt, L. = Loam, and C. = Clay. V. O. W. = Virgin open woodland, V. P. = Virgin pasture, M. = Meadow, P. = Pasture. V. F. R. = Virgin fence row, V. M. G. = Virgin "Maple grove," R. = Road side, C = Cultivated.

From these results it is seen that the soil which reddened blue litmus paper gave no CO₂ when boiled under reduced pressure either with distilled water or with dilute HCl, and that none of the other soils gave CO₂ with distilled water under reduced pressure except 4731, which contained a very large amount, of carbonates, while the acid soil gave more CO₂ when

¹ *Jour. Agr. Sci.*, 1905, 1-322.

² THIS JOURNAL, Aug., 1912.

³ The apparatus permits the use of a smaller amount of 4 per cent. NaOH for absorption of CO₂ and makes it convenient to titrate all of the solution rather than an aliquot, thus reducing the analytical error.

TABLE II, PART I—SURFACE SOILS 0-6 INCHES THAT REDDEN BLUE LITMUS PAPER. (SEE FIG. I)

Lab. No	Veitch test	Litmus test	Per cent. CO ₂		Per cent. Humus	Condition ²	Type ¹
			by Marr method	official method ¹			
4688	1	Acid	0	0.0242	1.50	C.	Mi. Sd
5081	2	"	0	0.0308	0.47	C.	Mi. Si. L.
4687	3	Sl. Alk.	0	0.0308	1.53	P.	Waverly Clay
4709	4	Acid	0	0.0341	0.91	C.	Mi. Sd.
4677	5	Acid	0	0.0352	1.62	C.	V. Si. L.
4681	6	"	0	0.0440	1.18	C.	Mi. C. L.
4680	7	"	0	0.0460	1.24	C.	"
4711	8	"	0	0.0462	1.47	V. F. R.	Sand
4734	9	Sl. Alk.	0	0.0462	1.01	C.	Mi. C. L.
4651	10	Acid	0	0.0484	1.56	M.	D. Gr. Sd. L.
4652	11	"	0	0.0484	1.79	M.	D. Gravel
5668	12	"	0	0.0484	3.03	C.	D. Sd. L.
4673	13	Sl. Alk.	0	0.0484	1.20	C.	V. Si. L.
4719	14	Acid	0	0.0506	1.61	C.	Mi. C. L.
4650	15	"	0	0.0506	1.52	V. M. G.	D. Sd. Gr. L.
4727	16	Sl. Alk.	0	0.0550	1.55	C.	Sandy L.
4655	17	Acid	0	0.0572	3.54	C.	D. clay
4663	18	"	0	0.0572	1.61	C.	Mi. C. L.
4690	19	"	0	0.0572	1.13	C.	Mi. Gr. L.
4640	20	Sl. Alk.	0	0.0594	1.88	C.	Mi. clay
4671	21	"	0	0.0594	1.50	C.	Wab. L.
4684	22	Acid	0	0.0594	1.57	C.	Mi. C. L.
4642	23	"	0	0.0616	C.	"
4643	24	"	0	0.0616	C.	"
4661	25	"	0	0.0616	1.93	C.	D. Sandy L.
4704	26	"	0	0.0660	2.04	C.	Blk. Sd. L.
4699	27	Acid	0	0.0680	1.21	C.	D. clay
4660	28	"	0.0022	0.0682	1.35	V. O. W.	D. Sd. L.
4639	29	Acid	0	0.0682	2.40	C.	Mi. C. L.
4662	30	"	0	0.0682	2.12	M.	Sd. L.
4641	31	"	0	0.0682	1.74	C.	Mi. C. L.
5279	32	"	0	0.0704	1.25	C.	D. Si. L.
4675	33	"	0	0.0704	1.50	C.	V. Si. L.
4695	34	"	0	0.0715	2.31	C.	Clyde clay
4665	35	Sl. Alk.	0	0.0726	1.34	C.	Mi. St. L.
4732	36	"	0	0.0748	1.79	M.	Mi. C. L.
4647	37	Acid	0	0.0770	1.38	M.	V. Si. L.
4654	38	"	0	0.0770	2.09	C.	D. Gr.
4658	39	Alk.	0	0.0770	1.93	C.	D. Sd. L.
4679	40	Acid	0	0.0792	1.62	M.	V. Si. L.
4733	41	Sl. Alk.	0	0.0814	2.49	C.	Blk. Sd. L.
4674	42	Acid	0	0.0814	2.17	V. F. R.	V. Si. L.
4715	43	"	0	0.0836	2.02	V. O. W.	D. clay
4736	44	"	0	0.0902	1.28	V. O. W.	Clay L.
4670	45	"	0	0.0902	1.82	C.	D. Gr. L.
4648	46	"	0	0.0946	1.57	C.	D. Gr. Sd. L.
4703	47	"	0	0.0957	2.63	V. O. W.	Mi. Si. L.
4644	48	"	0	0.0990	2.02	M.	V. Si. L.
4657	49	Sl. Alk.	0	0.1012	2.40	V. O. W.	D. clay
4721	50	Acid	0.0132	0.1034	1.44	R. V. F. R.	"
4683	51	"	0	0.1078	1.61	V. O. W.	M. C. L.
5283	52	"	0	0.1100	2.21	V. P.	"
4685	53	"	0	0.1100	3.44	C.	Waverly clay
4646	54	"	0	0.1166	1.71	V. O. W.	V. Si. L.
4706	55	"	0	0.1188	3.39	V. O. W.	Clyde clay
4718	56	"	0.0022	0.1320	3.24	V. O. W.	Wabash loam
4737	57	Alk.	0	0.1518	3.15	C.	Clyde clay

Average 0.0714 per cent. CO₂ = 3244 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 2—SUBSOILS 6-36 INCHES THAT REDDEN BLUE LITMUS PAPER. (SEE FIG. II)

Lab. No.	Veitch test	Litmus test	Per cent. CO ₂		Subsoil Soil No.	Condition	Type
			by Marr method	official method			
4686	1	Acid	0	0.0022	53	C.	Waverly clay
4710	2	"	0	0.0088	4	C.	Sand
4689	3	"	0	0.0088	1	C.	Sand
4745	4	Sl. Alk.	0	0.0110	67	C.	Silt loam
4720	5	Acid	0	0.0132	14	C.	Clay
4700	6	"	0	0.0132	27	C.	D. clay
5280	7	"	0	0.0198	32	C.	D. Si. L.
4645	8	"	0	0.0220	48	M.	V. Si. L.
4664	9	"	0	0.0220	18	C.	Clay loam
4691	10	"	0	0.0220	19	C.	Mi. Gr. L.
4672	11	"	0	0.0242	21	C.	Wab. loam
4649	12	"	0	0.0264	46	C.	D. Gr. Sd. L.
4682	13	"	0	0.0264	6	C.	Clay loam
4676	14	"	0	0.0319	33	C.	V. Si. L.
4659	15	Neut.	0	0.0330	39	C.	D. Sd. L.
4666	16	Acid	0	0.0792	35	C.	Mi. Si. L.

Average, 0.0228 per cent. CO₂ = 1036 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 3—SURFACE SOILS 0-6 INCHES THAT TURN LITMUS BLUE. (SEE FIG. III)

Lab. No.	Veitch test	Litmus test	Per cent. CO ₂ by		Difference	Per cent. humus	Condition	Type	
			Marr method	official method					
4708	58	Acid	Sl. Alk.	0.0011	0.1122	0.1111	2.88	V. O. W.	Clyde clay
4667	59	"	Alk.	0.0022	0.0726	0.0704	1.19	V. O. W.	Mi. Si. L.
4747	60	Sl. Alk.	V. Sl. Alk.	0.0033	0.0440	0.0407	0.97	C.	Silt loam
4722	61	Alk.	Alk.	0.0044	0.0902	0.0858	1.72	C.	Sand
4740	62	"	Neut.	0.0044	0.0704	0.0660	1.27	River T.	Clay
4746	63	Sl. Alk.	Alk.	0.0066	0.0462	0.0396	1.43	V. F. R.	Silt L.
4725	64	"	Sl. Alk.	0.0088	0.0968	0.0088	1.80	C.	Sd. C. L.
4701	65	"	Alk.	0.0110	0.1034	0.0924	3.35	C.	Sand
4724	66	Alk.	Sl. Alk.	0.0132	0.0770	0.0638	1.79	V. S. Y.	Sand
4744	67	"	Alk.	0.0132	0.0660	0.0528	1.31	C.	Silt loam
5085	68	"	"	0.0143	0.0528	0.0385	C.	Clay loam
4739	69	"	Sl. Alk.	0.0281	0.1496	0.1215	3.49	V. F. R.	Clay
4730	70	"	Alk.	0.0484	0.1232	0.0748	1.93	V. B. G.	Clay loam
4741	71	"	"	0.0506	0.2168	0.1662	6.48	Alluvial	Wabash loam
4751	72	"	"	0.0506	0.0814	0.0308	0.98	V.	D. clay
4712	73	"	"	0.0539	0.1210	0.0671	1.96	C.	Clay loam
4749	74	"	Sl. Alk.	0.0682	0.1210	0.0528	1.13	C.	Silt loam
5083	75	"	Alk.	0.0792	0.1540	0.0748	1.34	V. O. W.	Silt loam
5281	76	"	"	0.0946	0.1782	0.0836	1.50	C.	Silt
5087	77	"	"	0.2530	0.3630	0.1100	3.26	Blk. Swale	Clyde clay
4698	78	Sl. Alk.	Neut.	0.5632	0.6809	0.1177	1.88	V. F. R.	Clyde clay
4714	79	Alk.	Alk.	0.5720	0.6600	0.0880	1.23	V. F. R.	D. clay
4743	80	"	"	1.5220	1.8830	0.3610	6.56	V. Alluv.	Wabash loam

Average difference, 0.0912 per cent. CO₂ = 4144 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 4—SUBSOILS 6-36 INCHES THAT TURN LITMUS PAPER BLUE. (SEE FIG. IV)

Lab. No.	Veitch test	Litmus test	Per cent. CO ₂ by		Difference	Subsoil of surface		Condition	Type
			Marr method	official method		Soil No.			
4726	1	Sl. Alk.	Neut.	0	0.0572	0.0572	64	C.	Sd. C. L.
4728	2	"	Sl. Alk.	0	0.0132	0.0132	16	C.	Sd. L.
5082	3	Alk.	"	0	0.0176	0.0176	2	C.	Mi. Si. L.
5088	4	"	V. Sl. Alk.	0	0.0286	0.0286	68	C.	Clay L.
4705	5	Sl. Alk.	Neut.	0.0022	0.0253	0.0231	26	C.	Blk. Sd. L.
4723	6	"	Alk.	0.0066	0.0462	0.0396	61	C.	Sand
4738	7	Alk.	Sl. Alk.	0.0088	0.1012	0.0924	57	C.	Clyde clay
4656	8	Sl. Alk.	Alk.	0.0088	0.0396	0.0308	17	C.	D. Clay
4702	9	"	Sl. Alk.	0.0088	0.0242	0.0154	65	C.	Sand
4707	10	"	"	0.0088	0.0506	0.0418	55	V. O. W.	Clyde clay
4717	11	Alk.	Neut.	0.0110	0.0682	0.0572	..	C.	Wabash L.
4697	12	"	Alk.	0.0770	0.1331	0.0562	34	C.	Mi. Blk. C. L.
4742	13	Sl. Alk.	"	0.3652	0.4048	0.0396	71	Alluv.	Wabash L.
4748	14	Alk.	"	0.5522	0.6050	0.0528	60	C.	Silt L.
4731	15	"	"	2.0680	2.1010	0.0330	70	V. B. G.	Clay L.
4713	16	"	"	2.0900	2.1010	0.0110	73	C.	Clay L.
4750	17	"	Sl. Alk.	2.1030	2.1650	0.0620	74	C.	Silt L.
5086	18	"	Alk.	7.9090	8.0960	0.1870	77	Blk. Swale	Clyde clay

Average, 0.0477 per cent. CO₂ = 2167 pounds CaCO₃ per acre, 7 inches by official method.

boiled at 100° with distilled water than either 4722 or 4724, and that this was considerably increased for all soils on boiling at 100° with HCl. Sample No. 4731, which contained a very large amount of CO₂, gave nearly the same with acid under both conditions, viz., 0.08 per cent. higher for the strong acid at 100° C., which difference is not far from the average amount obtained from acid soils by boiling at 100° with HCl, as is seen from Table II.

Repeated experiments with other soils gave the same variations as are above shown. Only soils containing large quantities of carbonates gave any CO₂ when boiled with water alone under reduced pressure.

After this preliminary work was done it was decided to make the determination of CO₂ by both methods and compare these results with the litmus paper and Veitch qualitative tests.

For this work 114 samples of soil were used, representing eighteen different types, varying from light sands to heavy clays and from 0.47 per cent. to 6.56 per cent. of humus by the modified Grandeau method; 80 were surface soils, 21 of which were virgin soils from timber lands, fence rows or pastures; 34 were subsoils below the cultivated surface soils.

The litmus paper test was made by moistening the soil with boiled distilled water and making it into a stiff paste, a strip of blue and a strip of red azolitmin¹ paper were placed about an inch apart in a petri dish, covered with a piece of filter paper and the wet soil spread over the filter paper, other strips of red and blue litmus paper were folded and inserted into openings in the soils which were pressed against the folded paper so that when the paper was unfolded it presented a clean surface that had not been in direct contact with the soil. A third set of strips were placed on top of the soil and pressed firmly against it so the contact would be perfect; the cover was then placed on the dish and allowed to remain over night; the comparison was made with a moistened strip of neutral litmus paper. None of the paper was handled with the fingers.

The results were recorded in order of the degree of color change produced in the paper. There was very little difference in degree of color produced by the same soil for any of the methods of applying the paper, and it seemed that one method was as good as the other so long as the soil remained covered and the con-

¹ The best grade of azolitmin paper was used.

tact was allowed to continue for a sufficient time.

The Veitch qualitative test was made by shaking 10 grams of soil with 100 cc. of cold distilled water, free from CO₂, and allowing to settle over night or until sufficiently clear to pipette off 50 cc., to which was added a few drops of phenolphthalein; it was then boiled to about 15 cc. in a 150 cc. Jena beaker and the degree of color recorded, as very slightly alkaline,

that for all of these soils there is a wide variation between the two sets of results. In many cases acid soils give more CO₂ by the official method than alkaline soils, especially is this true of surface soils high in organic matter. In the case of subsoils there is a somewhat closer agreement. For soils containing large amounts of carbonates the differences are not very great for such quantities, but are of about the same magnitude as those obtained from soils giving no CO₂ by the Marr method.

TABLE III—LABORATORY NOS. OF SOILS IN WHICH VARIATIONS OCCURRED BETWEEN THE QUALITATIVE TESTS AND CO₂ BY MARR METHOD¹

Depth of sampling Inches	Soils alkaline by Veitch test which gave no CO ₂	Soils alkaline to litmus paper which gave no CO ₂	Soils neutral to litmus paper which gave no CO ₂	Soils acid by Veitch test which gave CO ₂	Soils acid to litmus paper which gave CO ₂	Per cent. of CO ₂ in soils by Marr method
0-6	4718	4718	0.0022
0-6	4721	4721	0.0132
6-36	4726	4726	0
0-6	4727	4727	0
6-36	4728	4728	0
0-6	4732	0
0-6	4733	0
0-6	4734	0
0-6	4737	4737	0
6-36	4745	0
6-36	5082	5082	0
14-24	5088	5088	0
0-6	4640	0
0-6	4657	0
0-6	4658	0
0-6	4660	4660	0.0022
0-6	4665	0
0-6	4671	0
0-6	4673	0
0-6	4687	0
0-6	4708	0.0011

¹ For other data on these samples see Table II.

Table III shows the variations which occurred between the litmus and Veitch tests and the CO₂ from these soils by the Marr method.

Samples 4718-4721 and 4660 were the only soils which were acid to litmus paper that gave any CO₂ at all (these results were checked and four determinations gave the same amount of CO₂). Sample 4718 is a virgin timbered soil overlying an alkaline subsoil containing CaCO₃; 4721 is a virgin soil from a fence row on a roadside and may have been contaminated with CaCO₃ in the road dust; 4660 was a virgin timbered soil; 4708, which was acid by the Veitch test and alkaline to litmus, was a virgin timbered soil, no subsoil being taken. With the exception of these four virgin soils, it is observed that all of the soils, which reddened blue litmus paper, failed to give any CO₂ at all.

Only three soils that react alkaline to litmus paper fail to give CO₂ and these are all subsoils which are only slightly alkaline. This alkalinity, as pointed out by Cameron,² may be due to the presence of certain minerals which give alkaline solutions by hydrolysis, independent of the presence of carbonates.

Of the 17 soils that were alkaline by the Veitch test and gave no CO₂, six were alkaline or neutral to litmus paper, the remaining eleven reddened blue lit-

¹ Bureau of Soils, Bull. 30.

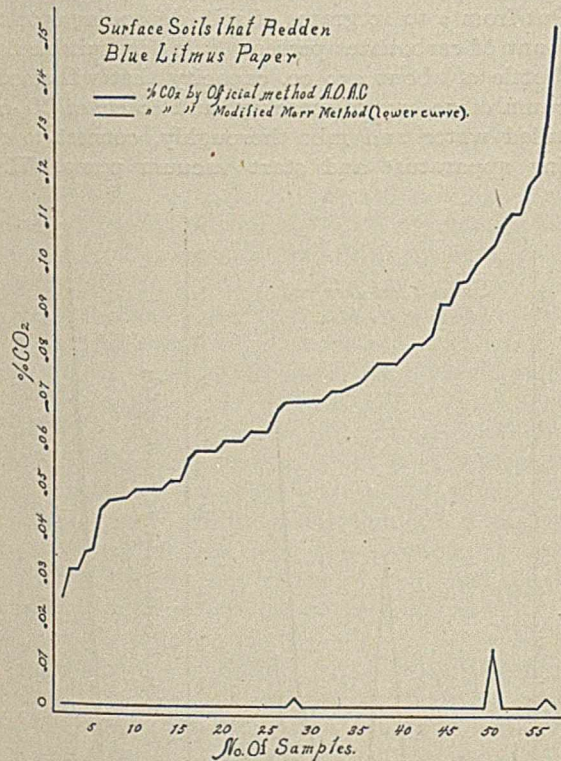


FIG. I

slightly alkaline and alkaline. If no pink color appeared, it was recorded as acid. All these tests were checked by two analysts.

These reactions were tabulated and compared with the CO₂ results obtained by the two methods as found in Table II:

From this table it is seen that there is a very marked agreement between the reaction of these soils and the CO₂ obtained by the Marr method, while there is little or no agreement with the official method.

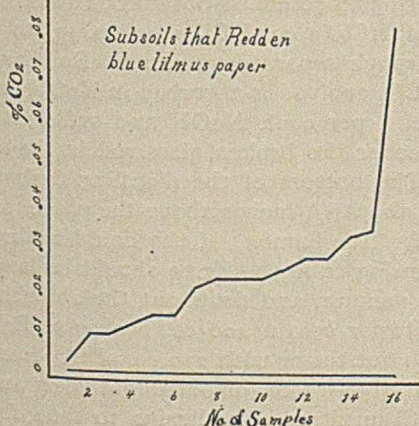


FIG. II

A comparison of the CO₂ by the two methods shows

mus. Some of these gave no alkaline reaction to phenolphthalein when the soil itself was boiled with water and the clear extract tested.

By inspecting Figs. I and II, in which the percentage of CO_2 by the official method is arranged in ascending series, it is readily seen that there is no regularity in the variations of the amount of CO_2 obtained by the two methods. By eliminating the three samples, 4718-4721 and 4660 (to which attention has been directed), the curve representing results obtained by the Marr method becomes a straight line for all soils that redden blue litmus paper, whether surface or subsoils.

For alkaline soils the results by the Marr method

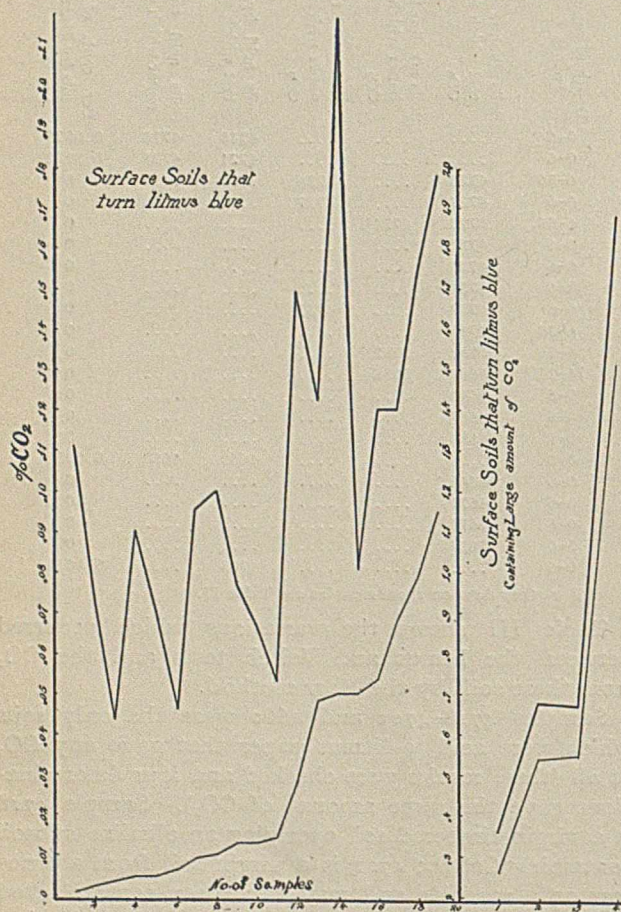


FIG. III

are arranged in ascending series. Figs. III and IV show that there is still no regularity in the variations of the two methods until the amount of CO_2 approaches 0.3 per cent., from which point the differences are not so noticeable, but are still of about the same magnitude as for soils giving no CO_2 at all.

As a rule, the differences between the two methods are greatest for virgin soils or soils containing large amounts of organic matter.

While no pot or field work has been done on these soils, observations made at the time of sampling and the agricultural history of the sections from which these samples were taken, point to the fact that there is a close agreement between their carbonate content and the productivity of the soils, especially as indicated by the clover yields.

THE METHOD FOR CO_2 IN SOILS

The changes made in the methods used by Marr are in the amount of 4 per cent. NaOH used, the titration of all of the solution instead of an aliquot, and the use of a different apparatus.

Repeated tests using c. p. carbonates and samples of soil justified these changes.

The method as used in this laboratory is as follows:

Put from 2 to 20 grams of soil (depending upon the amount of carbonates present) into any suitable flask or bottle of about 250 cc. capacity that will stand a vacuum of 70 cm. of mercury, add 80 cc. of CO_2 -free distilled water and mix thoroughly, connect to distilling apparatus¹ and start vacuum pump. When

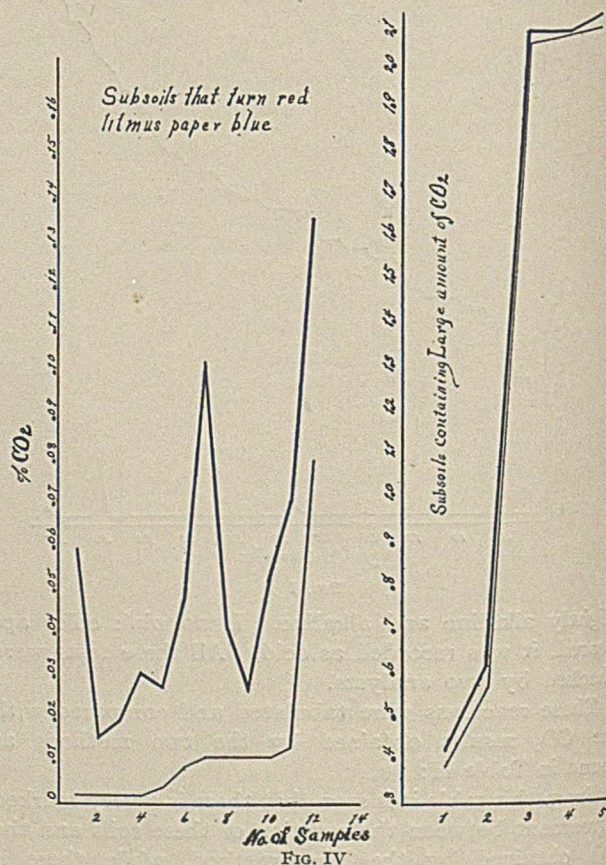


FIG. IV

the air has been removed from the apparatus and a vacuum of 65 to 70 cm. is obtained, run in 20 cc. of a solution of HCl (2 cc. HCl , 1.19 sp. gr. to 18 cc. of water) through separatory funnel. Boil for 30 minutes; the CO_2 evolved is absorbed in NaOH made from Na (25 cc. 4 per cent. NaOH and sufficient CO_2 -free water to cover the broken glass rod in the absorbing tower). The bottom of the distilling flask or bottle should be about $\frac{3}{4}$ inches above the gauze protecting it from the free flame. If the liquid is thrown into the condensing tube the flame should be lowered.

Relieve vacuum and draw out the absorbing liquid from the tower into a 400 cc. beaker or Erlenmeyer flask, wash out tower with 250 cc. of CO_2 -free distilled water, add about 1 cc. of phenolphthalein and run in normal HCl until red color begins to fade; finish this titration with $N/20$ HCl . When this end point is reached, add 2 drops of methyl orange solution (1

¹ THIS JOURNAL, 4, 611-612.

gram per 1000) and fill burette with $N/20$ HCl. Take no account of N or $N/20$ acid used in the previous titration. Run in $N/20$ HCl until the lemon color of the alkaline methyl orange just darkens to slight orange,¹ take reading of $N/20$ acid and subtract blank, which should be about 4 cc. 1 cc. $N/20$ HCl = 0.0022 gram CO_2 , 0.0028 gram CaO or 0.005 gram $CaCO_3$.

CONCLUSIONS

The boiling of soils with mineral acids at 100° C. (as pointed out by Cameron, Marr and others) decomposes organic matter and liberates CO_2 which is not present as carbonates and therefore the official method is of no value as a measure of carbonates in soils.

That if soils are boiled under reduced pressure at 50° C. with very dilute mineral acids no organic matter is broken up and the CO_2 evolved is all derived from carbonates.

That the litmus paper test, if properly made, is the best qualitative test we have for the presence or absence of native carbonates in soils from humid regions.

That some soils may give alkaline aqueous solutions, not due to the presence of carbonates but to the hydrolysis of certain minerals which exist in these soils.

That, although the reddening of blue litmus paper by soils may be due to the absorption of the base from the hydrolyzed litmus salt, the presence of native carbonates in a soil may either prevent this selective absorption or cause an interchange of bases to take place.

That if a native carbonate, capable of being decomposed by weak HCl at low temperatures, is present in a soil it is indicated by the bluing of red litmus paper when brought in contact with the moist soil.

That if there are no alkalis or basic materials, in a soil, which are capable of giving alkaline solutions, the absence of such substances will be indicated by the reddening of blue litmus paper.

That if these conclusions are correct, as is strongly indicated by the data already presented, there exists in soils which redden blue litmus paper a condition favorable to the formation of acids or acid salts which would unite with the base absorbed from hydrolyzed litmus and fail to return another base in its stead, thus producing the reddening of the indicator, even though it yields no H ions to a water solution. It is therefore possible that such a soil may be capable of producing a physiological effect similar to that produced by stronger acids which do yield H ions to aqueous solutions.

LABORATORY OF THE CHEMICAL
DEPARTMENT OF THE OHIO
AGR. EXPT. STA.

A CONTRIBUTION TO OUR METHODS OF DETERMINING NITROGEN IN HUMUS

By CHARLES B. LIPMAN AND H. F. PRESSEY

Received Sept. 30, 1912

So far as investigations on the subject have gone to date, nitrogen as nitrates still retains the importance

¹ It will be well for those not familiar with this titration to practice on solutions containing a little Na_2CO_3 . It will be necessary for each analyst to establish and adhere strictly to a constant end point for both indicators.

which must of necessity attach to an essential and very elusive element of plant food. While some plants may prefer to take up nitrogen as ammonia there can be but little question as yet that most plants prefer the nitrate, and we have further evidence that in the absence of such nitrate material the enforced absorption of ammonia by plants is apt to result in certain manifestations of disease due to the disturbance of their physiological mechanism. This, therefore, together with the fact which Hilgard has pointed out,² that *unhumified* organic matter, in his definition of the term, will not nitrify, would appear to invest the humus determination in soils by some method similar to that of Grandeau³ with primary importance in the chemical analysis of soils. Equal importance will, of course, attach to the nitrogen determination in humus since from what has been said above it is that, and not the total soil nitrogen, which may be depended upon to yield through nitrification an available supply of nitrogen to plants.

The general acceptance of the views above given has led to the prosecution of extensive studies looking toward the perfection of the method for determining humus in soils and the reader is referred for a discussion thereof to the recent work of Alway³ and his associates and to that of Kelley and McGeorge.⁴ But while much work has been done on the method of determining humus, but little or no systematic work has been done on the determination of nitrogen in the humus since it has always been assumed that the latest modifications of the Kjeldahl or Gunning method were as reliable for determining nitrogen in the humus as they were for determining that element in other substances. To obtain a more reliable and uniform method for this determination we have carried out a series of investigations in which some of the best known methods for the determination of nitrogen in humus were compared and the results of which we describe below.

HUMUS EMPLOYED IN THE EXPERIMENTS

In order to experiment with widely different kinds of humus we extracted soils of low, good, and very high humus content in accordance with the method outlined in *Circ. 6*, of the California Agricultural Experiment Station. The soils employed for this purpose were as follows:

No. 1. Light sandy soil from walnut orchard, Anaheim, California. Humus content 0.55 per cent.

No. 2. Silty clay loam derived from the State of Washington. Humus content 8.89 per cent.

No. 3. Tule soil from island in the Sacramento River. Nearly all organic matter. Humus content 28.7 per cent.

EXPERIMENTS ON THE DETERMINATION OF NITROGEN IN VARIOUS HUMUS SOLUTIONS

Portions of fifty cubic centimeters of humus extract were boiled with one gram of magnesium oxide in 500 cc. Jena Kjeldahl digestion flasks until no more ammonia was given off as indicated by a test with

¹ "Soils," Macmillan & Co., 1910, p. 359.

² *Circ. 6*, California Agr. Expt. Station.

³ *Bull. 115*, Nebraska Agr. Expt. Station.

⁴ *Bull. 33*, Hawaii Agr. Expt. Station.

litmus paper. The residue was then treated for the digestion of the nitrogen by the different methods whose relative efficiency was to be tested. All the methods given are so well known as to need no further description here. The last method, which was first suggested by Hibbard, as a result of some of his investigations on fertilizers, deserves brief description here, however, since it was published only recently¹ and because it has given by far the best results in our hands. The method of digestion as proposed by Hibbard consists in treating the substances to be analyzed with 30 cc. of concentrated H₂SO₄ until fumes of SO₃ begin to come off. There is then

I. The Hibbard method of digestion gives the highest amounts of nitrogen in all cases except one (see Soil No. 3), thus showing a more thorough digestion.

II. The duplicate and triplicate determinations show the best agreement when the Hibbard method is employed.

III. The digestion is carried out most rapidly by the Hibbard method and, particularly, much more rapidly than by the salicylic acid method which, in other respects, comes the nearest to the Hibbard method in yielding satisfactory results.

IV. In all the methods employed, considerable trouble with bumping was experienced except with

COMPARISON OF NITROGEN DETERMINATIONS BY DIFFERENT METHODS

Method of N determination employed	Soil No. 1			Soil No. 2			Soil No. 3		
	Time necessary to clear solution Minutes.	Nitrogen found Mg.	Per cent. nitrogen in humus	Time necessary to clear solution Minutes	Nitrogen found Mg.	Per cent. nitrogen in humus	Time necessary to clear solution Minutes	Nitrogen found Mg.	Per cent. nitrogen in humus
Wilfarth's method.....	25	{ 2.07 2.20 2.17	3.91	30	{ 7.31 7.21 7.07	4.86	40	{ 13.27 13.64 13.51	4.62
Gunning-Atterberg method.....	20	{ 2.62 2.34 2.31	4.40	25	{ 8.05 7.70	5.32	35	{ 13.05 13.66 13.87	4.71
Hibbard method.....	15	{ 3.29 3.10 3.33	5.89	20	{ 8.13 8.36	5.57	30	{ 13.94 13.66 13.87	4.82
Salicylic acid method.....	30	{ 3.10 2.87	5.44	40	{ 7.66 7.66 7.49	5.14	60	{ 14.28 14.21 14.10	4.95

added 12 grams of a salt mixture consisting of 10 grams K₂SO₄, 1 gram FeSO₄ and 0.5 gram CuSO₄, and the solution is digested until the nitrogen is all changed to ammonia. There follow results obtained by the use of humus portions equivalent in the case of Soil No. 1 to 10 grams of the soil, in the case of Soil No. 2 to 1.66 grams of the soil and in the case of the Soil No. 3 to 0.5 gram of the soil. The amounts of nitrogen found in milligrams are given in duplicate or triplicate and the percentages of nitrogen are calculated on the basis of the averages of these amounts. All other data are given in the table below:

In a comparison of the data set forth in the above table, and the experience had in the management of the various determinations we find:

the Hibbard method, in which the digestion proceeded rapidly and quietly in all cases, thus confirming the experience of Hibbard as reported in the paper above cited.

V. The manipulation included in the Hibbard method surpasses in simplicity and speed all the other methods tested, among which are those most commonly used to-day.

In view of the fact, therefore, that the Hibbard method is far superior to the others so far as both accuracy and speed are concerned, we must urge its use in all humus nitrogen determinations.

SOILS RESEARCH LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LABORATORY AND PLANT

THE MANUFACTURE AND PROPERTIES OF SUBLIMED WHITE LEAD²

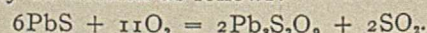
By JOHN A. SCHAEFFER

The manufacture of sublimed white lead, the commercial name for the basic sulfate of lead prepared by the sublimation process, depends directly upon the oxidation of galena, the sulfide of lead, when subjected to intense heat in an oxidizing atmosphere. The combustion under these conditions proceeds with violence resulting in the formation of a white sublimate, which, when purified, is known as sublimed white lead.

¹ THIS JOURNAL, 2, 463.

² Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

The reaction which occurs in this oxidation of galena may be written as follows:



This formula, Pb₃S₂O₇ or 2PbSO₄.PbO, is analogous to the generally accepted formula for the basic carbonate of lead—2PbCO₃.Pb(OH)₂. Commercial sublimed white lead, however, contains a higher percentage of lead sulfate than that required for the above theoretical formula. While the formation of the theoretical basic sulfate of lead is entirely feasible, its manufacture has not proved commercially advantageous. The conditions for the oxidation of the sulfide of lead are, consequently, so adjusted that a compound showing about 16 per cent. of lead oxide is ob-

tained. The conversion of a small percentage of the lead oxide, present in the theoretical basic sulfate of lead, to lead sulfate, undoubtedly results from a reaction between the lead oxide and the sulfur trioxide which forms from the oxidation of a certain amount of sulfur dioxide. A small percentage of zinc oxide is formed at the same time from the sphalerite, the sulfide of zinc, which is present in almost all non-argentiferous lead ores. It is maintained that the presence of about 6 per cent. of zinc oxide enhances the value of the pigment.

Coke of a hard compact variety is used as fuel, while iron, in the metallic form, and limestone serve as fluxing materials together with the silica present in the ore. Any metallic lead which forms from a reduction of the lead compounds by the coke, at the intense heat continually maintained in the furnace, is separated from the readily fusible slag by a difference in their specific gravities.

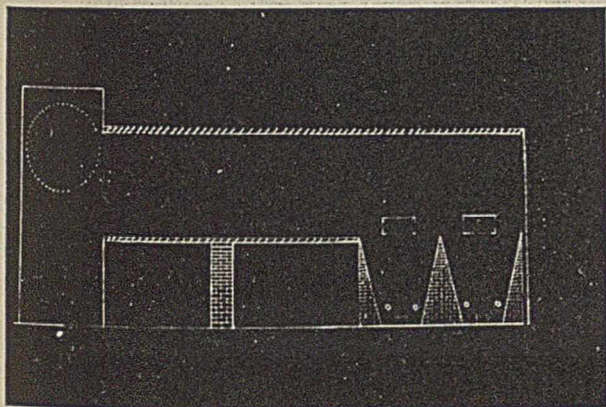


FIG. I.—DIAGRAM SHOWING LOCATION OF FURNACES IN RELATION TO COMBUSTION CHAMBER AND "BEEHIVE"

Blue Fume, the fume known commercially as sublimed blue lead, is frequently added to the charge. This fume is formed in the smelting of lead ores and is recovered by the bag room process. It is found to contain about 35 per cent. of lead oxide and about 50 per cent. of lead sulfate. This fume pigment, sublimed blue lead, is rapidly finding extended use as a paint pigment for the protection of iron and steel. Its composition renders it extremely valuable as a charge material and being a product of sublimation it is extremely reactive when subjected to the conditions found in the oxidizing furnaces.

The method of charging the furnaces varies with atmospheric conditions and the life and temperature of the furnace, charges being formulated to meet these conditions.

By following the charge from the raw materials to the finished products, the general working conditions can be best understood.

The oxidizing furnaces, two being considered a unit, consist of oval iron water-jackets, four feet in height, open at both ends, the upper end being five feet in length and three and one-half feet in width.

This water-jacket is securely built in a brick structure, on a solid brick base, and has a small opening in

front which serves as a tap hole for the continuous removal of slag and metallic lead and their separation by the difference in their specific gravities. An oxidizing atmosphere is maintained by blowing air through tuyère holes entering near the base of the furnace. The feed door of suitable size and form is placed at one side of the furnaces.

The brickwork surrounding the water-jacket or furnace proper is extended upward so as to form a large combustion chamber, which is in some cases water-jacketed.

Immediately upon feeding the charge into the furnace, the fire of which is maintained at a point of incandescence, the reactions previously described occur with great violence and the volatilized lead passes upward into the combustion chamber.

Suction is maintained by a powerful fan placed between the bag room and the "goose-necks" which draws the condensed fume onward through the cooling system, finally driving it into the bag room where it is deposited.

The cooling system is built so as to produce maximum cooling effect by the introduction of baffles which prevent the easy passage of the fumes into the bag room. After the fume has passed out

of the beehive, where it is condensed and purified, it is drawn through the "goose-necks," large inverted U-shaped pipes resting on hoppers, by the large suction fans and thence forced into the bag room.

The bag room is of a special type somewhat similar to those used in the collection of all fumes.

In the sublimed white lead bag room, however, are found three rows of hoppers (Fig. V), each hopper carrying 24 bags. The pressure of the fan forces all the gas through the cloth of the bags, while the sublimate is deposited. Occasional shaking throws the fume into the hopper where it is packed for shipment.

Sublimed white lead, as it is removed from the hoppers, is white in color. Much fume, however, which is unsatisfactory and not suited for use in the various arts, is deposited in the portion of the cooling system preceding the suction fan. This fume is contaminated with a small percentage of coke, ash and other impurities, and being of a higher specific gravity than pure sublimed white lead it is readily deposited before reaching the fan, by a careful adjustment of the suction. The fume becomes darker in color the nearer the approach to the furnace. As a charge material the sublimate is excellent, owing to its very finely divided condition.

Sublimed white lead, being a fume product, consists of very fine amorphous particles, in size about

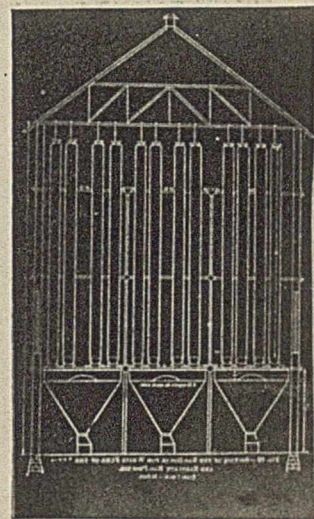


FIG. II.—DIAGRAM SHOWING ARRANGEMENT OF BAG ROOM

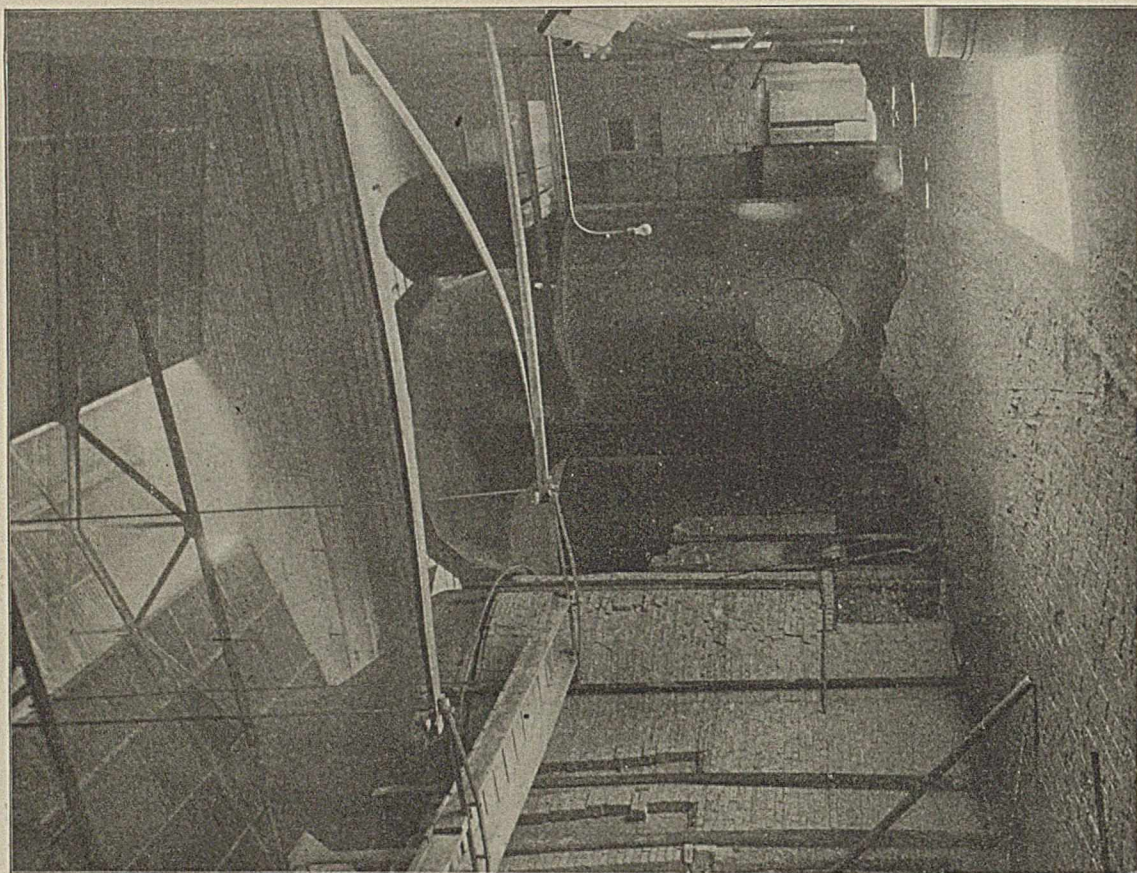


FIG. IV.—"BEEHIVE" WITH "GOOSE-NECKS" IN THE DISTANCE

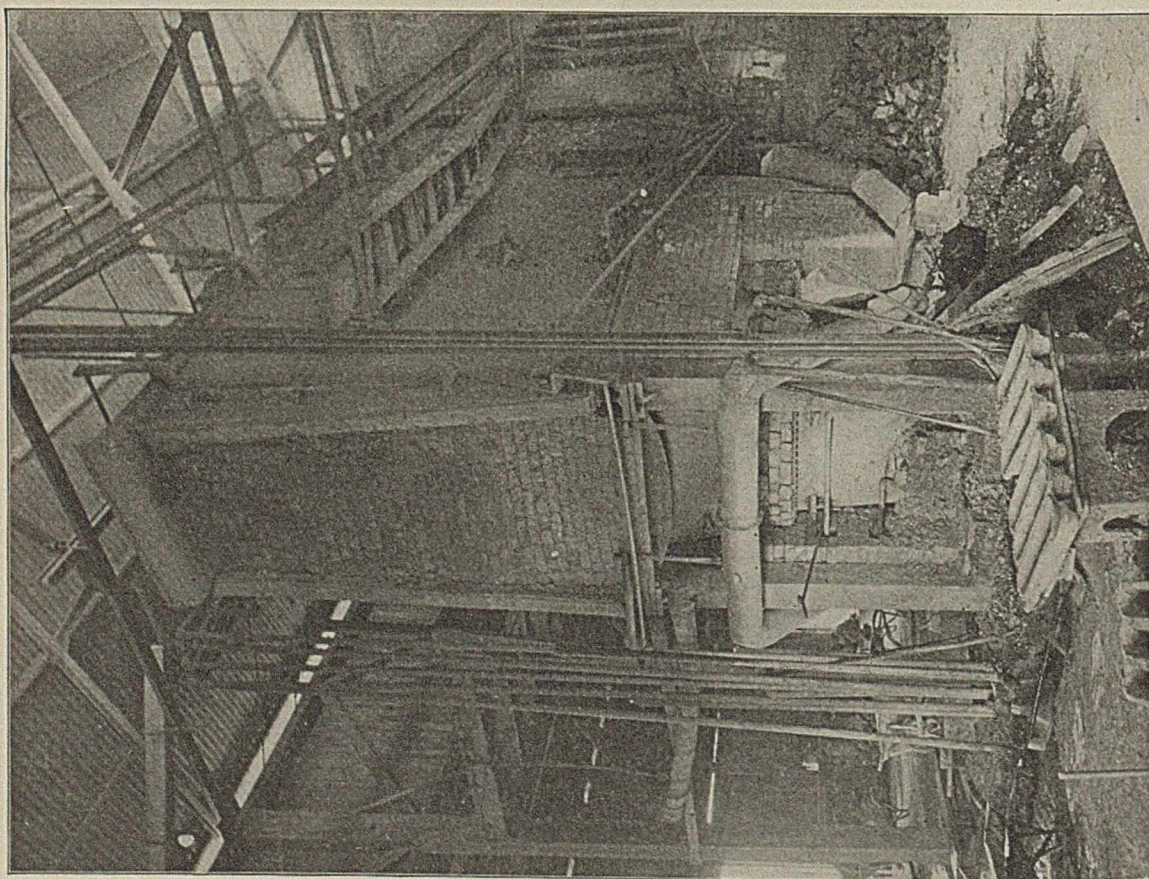


FIG. III.—FURNACE FOR MAKING SUBLIMED WHITE LEAD. COMBUSTION CHAMBER ABOVE. TROUGH FOR SEPARATION OF METALLIC LEAD FROM SLAG IS IN FRONT OF FURNACE

one thirty-five thousandth of an inch in diameter. Its specific gravity is found to be 6.2.

In composition it shows approximately 78 per cent. of lead sulfate, 16 per cent. of lead oxide, and 5.5 per cent. of zinc oxide. That the lead oxide present is chemically combined as a basic sulfate of lead, the sulfate of lead present in excess of the amount required for the theoretical formula being present as neutral sulfate of lead, is held by practically all authorities. Chevalier claims the formula of $Pb_3S_2O_9$ for the fume resulting from a furnace roasting lead sulfide.

According to Toch,¹ we find that "A mixture of precipitated lead sulfate, litharge and zinc white in approximately the proportions found in sublimed

est difficulty. It shows only slight darkening in an atmosphere containing appreciable amounts of hydrogen sulfide gas. When used in colored paints containing chemically reactive tinting materials, it exhibits chemical inertness. The tinctorial power and opacity is directly lowered with a decrease in the percentage of lead oxide.

When chalking is noted in paints containing high percentages of sublimed white lead, it is found to differ from that noted in the case of other white lead pigments. According to Holley,¹ we find: "When ordinary white lead begins to chalk vigorously, it will be found that the paint film has lost its elasticity, and has become brittle and friable throughout; also,

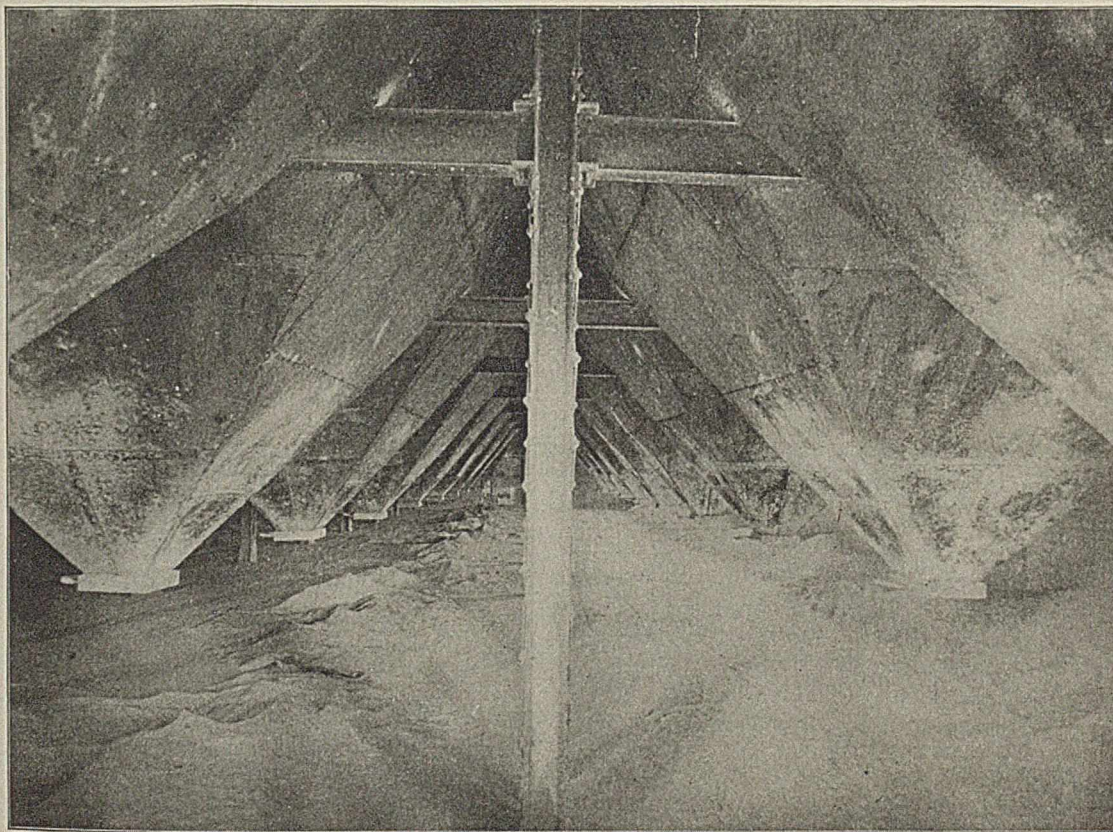


FIG. V.—HOPPERS INTO WHICH SUBLIMED WHITE LEAD FALLS FROM BAG ROOM

lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed white lead, when ground in raw linseed oil, takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for re-painting in twelve hours, because lead sulfate is a fair drier and lead oxide a powerful one. The oxy-sulfate having the same composition, behaves totally different from the mixture." A mixture of the neutral lead sulfate with two per cent. of sublimed litharge, the finest and palest oxide of lead yet prepared, shows a yellow color not approached by any sublimed white lead yet made.

When sublimed white lead is subjected to the heat of the blowpipe it is reduced to metallic lead, when intimately mixed with charcoal only with the great-

est difficulty. The pigment, in common with other white lead compounds, finds its greatest value when compounded with zinc oxide and a small percentage of inert pigment of a crystalline nature, as these pigments tend to overcome those factors which militate against the use of the pigment alone.

Sublimed white lead is a pigment extensively used in the compounding of the finer grades of rubber goods.

¹ "Chemistry and Technology of Mixed Paints," Maximilian Toch, p. 19.

¹ "Zinc and Lead Pigments," Holley, p. 115.

The pigment has been found to practically inhibit corrosion on iron and steel even after long exposures, and ranks favorably with all other pigments yet prepared for the elimination of this decay. In consequence, it is rapidly finding its predicted place among paint pigments not only as a protective coating for wood but as a preservative for iron and steel.

PICHER LEAD CO.
JOPLIN, MO.

A NEW FORM OF LABORATORY EXTRACTION APPARATUS¹

By A. E. PERKINS

Received October 25, 1912

The great variety of extraction apparatus now on the market would seem at first thought to supply a form adapted to any purpose; yet, in selecting apparatus for continuous use in a laboratory where large numbers of extractions must be made, one is impressed with the fact that all these forms have in common some of the disadvantages enumerated below.

Most forms of extraction apparatus are very complicated, very expensive and very frail. Nearly all forms have two joints of the cork, ground glass or mercury seal type. These are sources of endless breakage trouble and annoyance, besides furnishing an

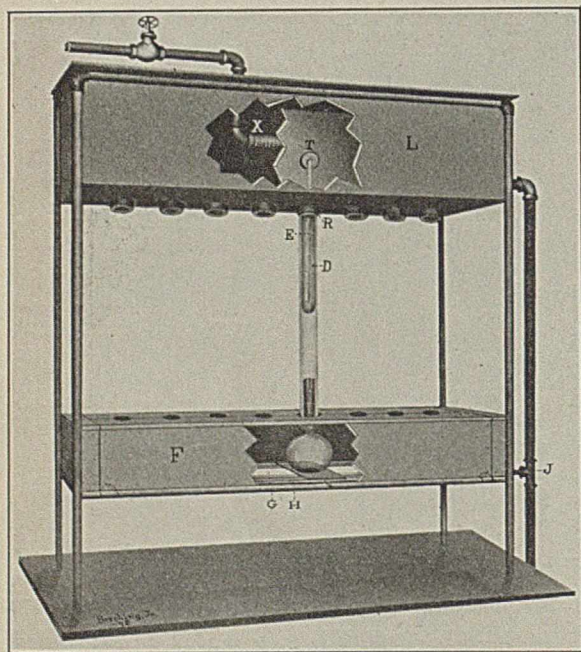


FIG. 1

easy means of contaminating sample or solvent with water leaking from or condensing on the supply pipes. Nearly all the common forms of extraction apparatus must be supplied with water under pressure, which must ordinarily be conveyed to the condenser through rubber tubing. This rubber tubing may frequently break or leak and flood the laboratory, or kink and shut off the water supply; moreover, to keep it in good condition requires continual care and expense.

Efforts by the writer to eliminate certain of these defects from an apparatus to be used in this laboratory

have resulted in the construction of the form of apparatus which is here described.

The frame supporting the apparatus (Fig. 1) is of $\frac{1}{2}$ inch metal tubing and has approximate dimensions of $36 \times 32 \times 8$ inches, accommodating 8 extraction flasks which are placed $3\frac{1}{2}$ inches between centers.

The extraction flask A (Fig. 3) is flat bottomed and has a diameter of $2\frac{3}{4}$ inches and a height of 2 inches to the base of the neck; the constricted portion of the neck B has height and diameter of about

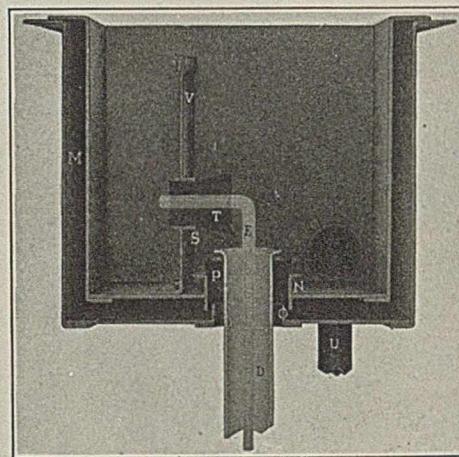


FIG. 2

one-half inch each; the large upper portion of the neck C has a diameter of $1\frac{1}{8}$ inches and a height of 12 inches. The condenser D is merely a test tube of special shape (9 inches \times $\frac{7}{8}$ inch). The small glass tube E has a diameter of about $\frac{3}{16}$ inch. All glass parts are of rather heavy German glass. The dimensions will accommodate any extraction tube up to 5 inches in length and one inch in diameter. A perforated porcelain, or aluminum plate is used to support tubes of small size.

The box F (Fig. 1), enclosing the lower part of the extraction flask, is of sheet metal about 4 inches high, the front, back and top being hinged so that they can be dropped out of the way, leaving the bottom of the box as an open platform when the flasks are being adjusted. The bottom of this box has an opening, G, three inches wide and extending the entire length of the box, except for two inches at either end. Heat is supplied by steam passing through a $\frac{1}{4}$ inch lead pipe, H, which makes three circuits of the box, being separated from the bottom by a layer of asbestos board. The valve controlling the flow of steam is not shown in the drawing. The $\frac{1}{4}$ inch lead pipe carrying the exhaust steam enters the waste pipe through a Tee joint, J, and extends downward 4 or 5 feet, completely condensing the exhaust steam.

The extraction flask when in position is supported directly over the opening G by a strip of heavy sheet copper 3×7 inches in dimensions, the ends of which rest on the steam heating coil, the copper strip serving also to conduct heat to the flask. When the flask is being put into or taken out of position, the copper

¹ Drawings by Mr. Wm. P. Beeching, Jr.

strip is withdrawn and the flask lowered through the opening G until clear of the condenser D.

The supply tank L (Fig. 1) for the test tube condensers consists of two sheet metal tanks placed one inside the other, M (Fig. 2), and separated by an air space. The bottoms of both tanks are provided with collared holes placed $3\frac{1}{2}$ inches between centers, the collars for the inside tank N (Fig. 2) being $1\frac{1}{2}$ inches in diameter and extending downward, those for the outside tank being one inch in diameter and extending upward into the tank thus overlapping as shown.

The test tube condensers are fitted into the collars of the inner tank with rubber stoppers, P (Fig. 2), being wound with fat free paper or cotton to make a close joint with the outer tank O and with the top of the extraction flask R (Fig. 1). The inner tank has a rim $\frac{3}{4}$ inch wide extending entirely around it; this rests on the top of the outer tank and thus en-

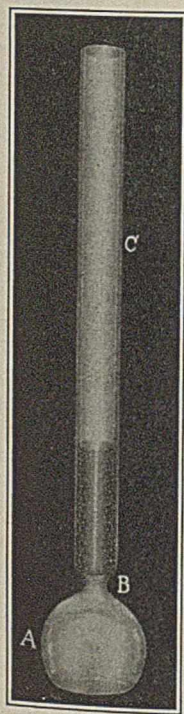


FIG. 3

encloses the air space between the two. The inner tank is provided with a partition, V, running lengthwise about two inches from the back wall of the tank, the top of the partition being an inch lower than the top of the tank. Collared holes are provided in the partition S (Fig. 2) two inches above and directly opposite the holes in the bottom of the tank; into these are fitted by rubber stoppers, S and T (Fig. 2), small glass tubes bent downward and extending nearly to the bottom of the test tube condensers as shown in Fig. 1. Water from the supply pipe enters the inner tank back of the partition and when its level has risen above the ends of the glass tubes, flows through them into the test tube condensers which overflow into the front chamber of the inner tank. Any excess of water will flow over the partition.

The water supply pipe is narrowed to a $\frac{1}{4}$ inch opening and provided with a hood as shown in Fig. 1; and the waste pipe U which is jointed to the inner tank by means of a rubber stopper is $\frac{3}{4}$ inch in diameter, thus eliminating the danger of flooding. By closing the waste pipe and allowing the water to stand 3 or 4 inches deep in the tank practically complete condensation of ether is secured for an indefinite period without running water when the room temperature is not unusually high.

Rapid and complete extractions are secured with this apparatus. Fat determinations are most conveniently made by difference, though the flask has no re-entrant surfaces to prevent complete transfer of the extract to another container for direct weighing.

Most of the faults enumerated above have been avoided in this apparatus. Joints of all kinds have been eliminated from the extraction apparatus proper.

No pipes for distributing water to the condensers and no troublesome rubber tubing connections are needed. Contamination of sample or solvent by water has been made nearly impossible. The glassware costs less than one-fourth as much as most other forms of extraction glassware, and being simpler and stronger it is less liable to breakage.

LABORATORY OF DEPARTMENT OF DAIRYING
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER

A DEVICE FOR CONTROLLING SMALL ELECTRIC FURNACES¹

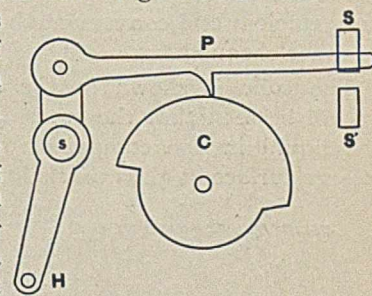
By CHARLES BURTON THWING

The plan described herewith for maintaining any desired temperature in a small electric furnace was devised for use with a 10 kilowatt carbon plate resistance furnace, for which direct current only was available.

It is usual to employ alternating current for such furnaces, reducing the voltage as the resistance of the furnace falls with the rising temperature.

Where direct current is used, the control is usually effected by means of a rheostat, which, of course, wastes a considerable portion of the energy. The present plan dispenses with the use of a rheostat, by automatically opening the circuit once a minute and closing it after an interval regulated at will.

The control is effected by means of a small motor, which drives, by small gears, a cylindrical cam, C, 250 mm. (9.87") long and 50 mm. (1.97") in diameter, the cylinder being cut away on a taper from 350° at one end to 0° at the other. The pawl P is carried on a screw, s, which can be turned by the handle H to set the pawl quickly and accurately to any desired position. When the pawl is resting upon the cam, the control switch S is closed. This automatically closes the clapper switch carrying the current; when the pawl drops, the control switch S' is closed, opening the clapper switch and cutting off the supply of energy from the furnace.



ELECTRIC FURNACE CONTROL

It is evident that the fractional amount of time during which the current is supplied to the furnace varies with the position of the pawl on the cam. While heating the furnace, the automatic switch is at rest; when the desired temperature has been attained, the motor which actuates the switch is started and the cam set to the position which has been found by trial to furnish the energy required to balance the losses by radiation. The pawl may be set with ease to within 1 mm. (0.03937"), which is, of course, a finer adjustment than is required.

The control of the furnace is further effected by placing in series with the carbon resistance an auxiliary resistance of 0.2 ohm of nichrome tape, which in-

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

creases to 0.3 ohm at the maximum temperature. The furnace is operated at 1300°C . (2372°F .), and since this is too high for the nichrome to withstand permanently, the latter is placed in the base of the furnace, where the temperature does not exceed 1100°C . (2012°F .). The increase of resistance of the nichrome with the rise of temperature tends to offset, in some measure, the diminishing resistance of the carbons, and so to prevent any accidental overheating of the furnace in case of failure of the operator to look after the adjustment of the controlling device.

The chief advantage of this plan over the rheostat is in the saving of energy. All the energy consumed is delivered to the furnace, except the small amount (about 50 watts) required to run the motor, and the much smaller quantity required to actuate the switch.

PHILADELPHIA, PA.

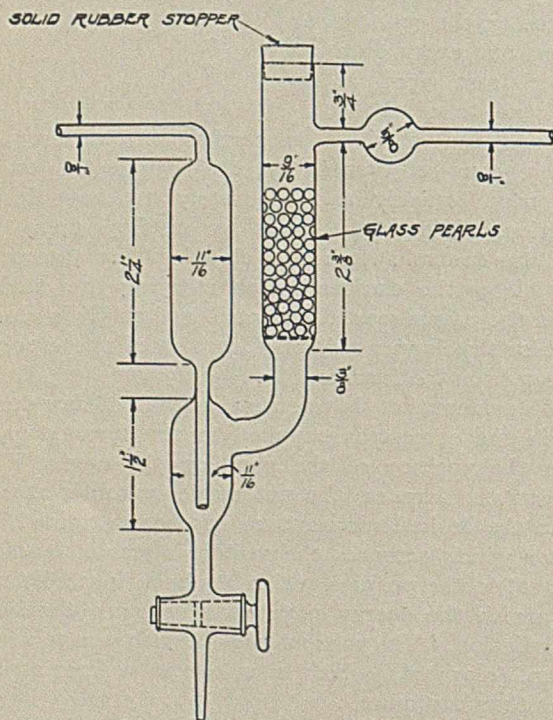
GAS BUBBLE AND WASHING TUBE FOR COMBUSTION APPARATUS

By H. E. SMITH

Received October 21, 1912

For several years I have used in combustion apparatus and for similar purposes a certain form of gas bubble and washing tube which has proved so very efficient and convenient that it may be of interest to other chemists.

The tube is shown in the accompanying sketch. It will be seen that the entering gas bubbles through the liquid in one compartment, then is exposed to a large surface of glass pearls in another compartment.



The especial feature of the tube is that the spent liquid may be drawn out and the tube refilled without breaking the connections with adjoining apparatus

or removing the tube from the train of apparatus. The spent liquid is drawn off by means of the stopcock after which the tube is recharged by removing the rubber stopper at the top and running in the proper quantity of fresh liquid from a pipette. It first moistens the pearls, then accumulates in the lower compartment.

LAKE SHORE & MICH. SOUTHERN RY. CO.
COLLINWOOD, O.

A MODIFIED EXTRACTION APPARATUS

By G. M. MACNIDER

Received October 18, 1912

While there are quite a number of extractors now on the market for determining fat in solid substances, with each form there is some feature which is not entirely satisfactory when a large amount of routine work is to be done.

The Soxhlet and Knorr forms are probably most generally used. The siphon principle of the Soxhlet apparatus has been found to be most satisfactory for general work, but the cork or ground glass joints of this apparatus cause considerable trouble in setting up the apparatus and are frequently the cause of the loss of large amounts of ether. The Knorr form is superior to the Soxhlet in that it requires about one-third the amount of ether for an extraction and has only one joint, which is a mercury seal, thereby preventing the loss of ether. But the percolation principle of the Knorr is unsatisfactory on account of the difficulty in preparing satisfactory asbestos filters. The modified form described below was designed to combine the desirable features of the Soxhlet and Knorr forms.

The apparatus consists of a small siphon extraction tube (Fig. I) which fits into the Knorr adapter in place of the percolation tube used in the regular Knorr apparatus. The extraction tube is 8 cm. long and 2 cm. in diameter. The siphon is sealed into the bottom and rises to within 1 cm. of the top of the extraction tube. The details will be apparent from the cut. The sample to be extracted is contained in a S. & S. extraction thimble which fits closely into the extraction tube. In this laboratory, extraction thimbles 19×90 mm. are used and the thimbles trimmed down to a height of 80 mm. to make them flush with the top of the extractor. The extraction tube is shown in place in Fig. II.

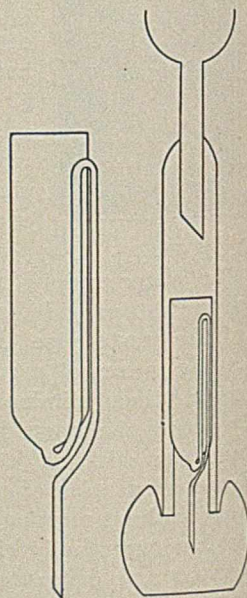


FIG. I

FIG. II

As will be seen from the above, the siphon principle of the Soxhlet apparatus has been combined with the desirable features of the Knorr apparatus. As the extraction tube is small the extraction is done very rapidly so that the apparatus is well adapted to both

commercial work where the extractions must be done in a short time and to more accurate scientific work where the substance is extracted for a longer time.

A set of twenty of these extractors has been in use in this laboratory for about six months and has proved entirely satisfactory with a variety of substances.

FEED AND MICROCHEMICAL LABORATORY
NORTH CAROLINA DEPARTMENT OF AGRICULTURE
RALEIGH

A REFLUX CONDENSER

By S. W. WILEY

Received October 25, 1912

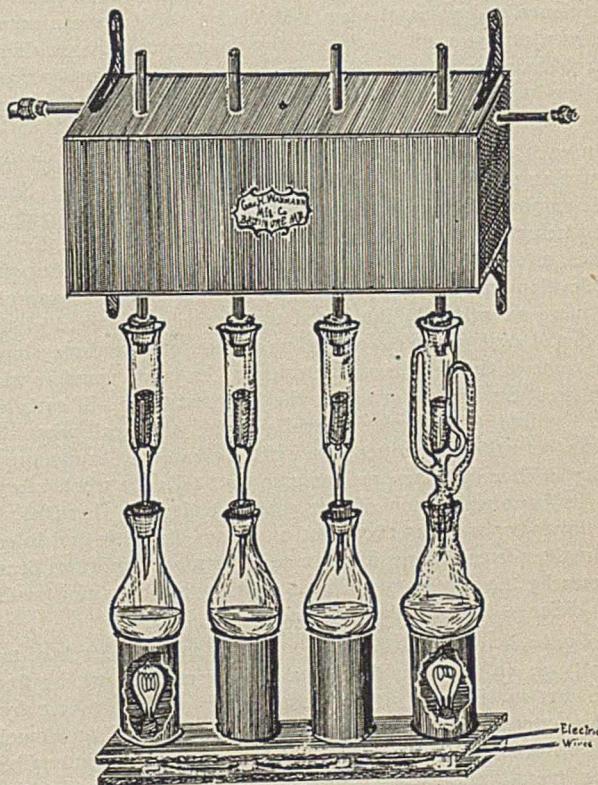
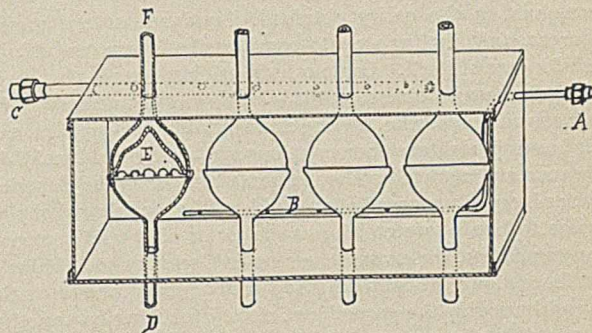
The piece of apparatus discussed in this paper was designed because of the small space occupied by it and the degree of efficiency obtained by its use in comparison with other types now on the market.

This condenser as shown has been used by Wiley & Company's laboratory and has given great satisfaction. We have found it indispensable for extraction with ether or other solvents or for any purpose where a reflux condenser can be brought into use. The cuts show clearly the construction of the various parts and, from a close inspection of the cuts, an adequate idea of the large condensing surface that can be obtained in comparison with the size of the water jacket. The condensing tubes are of block-tin tubing and on entering the water jacket are connected to bell-shaped condensers of spun copper. On entering the bell which is composed of two sections, the uncondensed ether passes through perforations and is condensed on the upper surface of the bell. The condensing surface of this arrangement is over 120 square inches in comparison to the straight tube usually used, two feet being the length that is ordinarily used with an internal diameter of $\frac{3}{8}$ inch which would have a condensing surface of about 25 square inches. The water inlet is so arranged that the water bubbles up and surrounds every portion of the condenser, and by this scheme we have the condensing surface continually exposed to fresh, cold water thus insuring continual condensing of the solvent with a minimum loss.

To this condenser any form of extraction apparatus may be connected and in this laboratory a special form is used, which is simple in construction and at the same time efficient.

For heating the solvent we use the scheme shown

below. The apparatus shown has two decks thoroughly insulated and with a two-inch air space between decks as a safeguard to overheating. The heating is furnished by 16 c. p. incandescent bulbs and a spun



cup, insulated on the outside to prevent radiation, surrounds the bulb and forms a rest for the extraction bulb.

ANALYTICAL LABORATORIES
WILEY & Co.
BALTIMORE

ADDRESSES

TAR DISTILLATION IN THE UNITED STATES—GENERAL DEVELOPMENT AND RECENT PROGRESS¹

By R. P. PERRY

INTRODUCTION

One feature of the general conservation movement which has attracted much attention in recent years is the estimated use and available supply of coal. For years our household and factory fires have been burning cheerfully—although in many cases rather smokily—and we have had an optimistic feeling that our

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

coal mines were inexhaustible. Even now fuel is so plentiful and comparatively cheap in many parts of the country that a large portion of the public forgets that there may be a cold tomorrow. If we travel by night through the Connellsville section we see the glare from thousands of beehive ovens light up the sky and throw picturesque shadows on the hills, but if we study the careful and interesting reports of the United States Geological Survey, we may well be amazed at the apparently reckless annual waste of millions of dollars worth of by-products—gas, ammonia and tar—from these ovens, when converting bituminous coal into coke for the great iron and steel industry. At the same time,

those who are familiar with the conditions abroad wonder why they see there so many orderly piles of coal briquettes utilizing the coal dust or slack with a coal tar pitch binder, while in certain regions here they see abandoned culm banks. The explanation is as indicated above—the past and present generation living for themselves on the easily obtained abundance of our mineral resources, and, if they stop to consider the future, assuming it will take care of itself. Some caustic criticism has been directed at American wastefulness, and it is by no means undeserved, but our foreign friends, who, having more slender coal supplies, raise their hands in righteous horror at our methods, should make due allowance and remember that in some directions the American traveler is equally amazed at the evidence he sees abroad of what appears to him a waste of human labor or of special materials. I can remember, for example, seeing in Germany some miles of solid fence along the railroad made of abandoned steel cross-ties, one end buried in the ground, set closely touching one another. We would hardly understand such fence construction from our experience and point of view. Similarly, the American manufacturer, accustomed to labor-saving devices at home, is almost speechless when he sees the army of porters cumbrously transporting luggage from boat to dock and *vice versa* at the European ports.

In each case there is sure to be some reason, although not always an adequate one, why conditions are as they are. Some little emphasis is laid on this point as it rises again and again in considering the development of the tar industry in the United States, as it inevitably must be considered in comparison with the development abroad, particularly in Germany. For example, the more scientifically interested traveler who has read of the wonderful coal tar dyes, colors, medicines, etc., and may have seen some of the very large factories in Germany, wonders why such products are not made in the United States. If satisfied with the first tabloid answer available, he will recall what the popular scientific magazines have written about the German superiority in chemical lines, and assume that tells the whole story. The brilliant reputation of our good friends, the Germans, is certainly very well deserved, but numerous domestic and international trade conditions have an equal or more important bearing on why the development of the industry has been along radically different lines here and abroad.

Going back to the initial fact that many million barrels of tar literally go up in smoke from our beehive coke ovens, we find there was in the past a well-defined fear of undertaking by-product ovens for several reasons. In the first place, it took much time to overcome the incorrect feeling that for some intangible reason metallurgical coke was better when made in beehive ovens. Also it was feared there would not be a market for the tar product which would be sufficiently large and remunerative. Both of these fears have now been overcome, as the successful use of by-product coke has become a fact in the most progressive furnaces, and in general the tar industry has taken up the greatly increased production.

Successful working up of the tar commercially here depends upon finding a profitable use for its main constituent, pitch, as there has been a much greater demand for the oils and the products derived from them than our domestic supply. The foreign use of pitch is mainly as a binder for coal dust or slack in making briquettes. There has recently been a very appreciable development of briquetting in certain sections here, but a curious argument in a circle is still heard at times. On the one hand, some coke operators have said there was no market for additional tar because there was no briquette industry and at the same time briquetting interests have regretted there was no assurance of an adequate supply of pitch binder because the limited output of tar distillation went to make pitches for other purposes which would bear a higher price. Between the two stood the tar distillers, ready and anxious for additional business, but as usual

there were other economic conditions having a most important influence.

In many places bituminous lump coal is still so comparatively cheap and abundant that briquettes could not compete and the market for domestic briquettes from anthracite dust is also somewhat limited. In some cases the geographical location of tar production and possible pitch consumption are so far apart that railroad freights are an insuperable barrier.

Another present and potentially very large use for tar products is in making bituminous road binders, as covered in other papers. I will only mention in passing that although this development in the United States is extremely satisfactory, yet there are very large supplies of petroleum products and residues designed for road work at low prices, whereas these conditions are reversed abroad, particularly in Germany. In fact, the great increase of road tar abroad has tended to divert much tar, leaving a shortage in the briquette pitch field.

As regards dyes, colors, medicines, special chemical products, etc., derived from coal tar, the conditions are peculiar. Most of these are derived from benzol, phenol, cresol, naphthalene and anthracene. Figured on the original tar these total only a relatively small percentage. Further, the finer products require numerous intermediate steps, involving more or less labor, as well as extensive chemical treatment with acids and alkalis. The price of labor abroad, including trained chemists, would probably average not more than about half that paid in the United States. The question as to what the smaller wages will purchase relatively in the way of rent, food, clothing, etc., is an interesting economic study, but does not alter the fact that to the manufacturer the labor costs very much less and enables him to produce cheaper in this respect. In many cases, also, he has an advantage in cheaper chemicals, which play a very large part in the cost of the finished products, running from about fifty per cent. upwards. Another most important feature is the patent situation. Many of the finer products derived from coal tar are covered by United States patents held directly or indirectly by a small group of German interests. Dr. Bernard Herstein has recently analyzed this situation in an interesting way.¹ Perhaps one most essential point is that existing United States patent law (differing from that of most foreign countries) permits patenting of the product as such as well as any particular means of production, and further, there is no requirement that the product be made or the process used in the United States. In other words, the German group can and does control a large number of United States patents on these products, and having this protection it is under no necessity of employing American labor or capital in manufacturing here, but can ship to this country from Germany or elsewhere, subject only to tariff regulations. The injustice of a similar situation has recently been recognized by Great Britain which adopted a compulsory working act, with the result that many foreign firms promptly built factories in England. The matter is very important in connection with the features mentioned, producing lower manufacturing costs in Germany. It seems probable, however, that with due justice to inventors, a proper revision of the patent laws will be accomplished before long.

One further rational explanation of why these finer products have not been produced here is that generally there have been uses for the crude or semi-refined products here which netted considerably more than the fine products would have secured. Naturally the tar industry has developed along the lines of least resistance, but already a beginning has been made here in the direction of the finer products, and many of these can be available as fast as there is a demand at prices permitting their manufacture under our conditions. Wherever mechanical handling and machinery plays an important part the United States probably has some advantage.

¹ Address before Society of Chemical Industry, New York, April 19, 1912.

SOURCES OF TAR, AND ESTIMATED QUANTITIES

In the discussion so far, I have referred only to the supply of tar from by-product coke ovens, as this is much larger at present than gas works tar and growing much more rapidly. The earlier coke ovens were built near the mines and steel works in Pennsylvania, but they have followed the blast furnaces as these have moved to the large distributing centers—it having been found better to haul the coal to such points instead of the coke. Such, for example, is the recent very large development near Chicago, there being by-product ovens at Gary, Joliet, South Chicago and Milwaukee. More recently, under peculiarly favorable conditions of supply of raw materials for iron and steel manufacture, some large coke oven plants have been erected near Birmingham, Alabama. There are many others distributed throughout the eastern half of the United States, some of them located where they can supply illuminating gas to large cities, and others use their surplus gas in open hearth furnaces or other parts of the steel plant. As distinct from by-product ovens, the gas works are located always in the cities, the largest producers of gas works tar being in New York, Chicago, Philadelphia, etc. Most of these gas works produce both coal tar and water gas or oil tar. The differences of quality will be considered later. In some sections of the United States the abundant and cheap supply of natural gas has temporarily, at least, made the operation of gas works financially impracticable.

It is somewhat difficult to get complete data of production of tar, especially of the gas works grade, but it seems probable that, including coke oven and both kinds of gas works tar, the 1912 production in the United States may not be very far from 165,000,000 gallons, of which about two-thirds is coke oven tar. In comparison with this, it has been estimated¹ that if the remaining beehive ovens were converted to by-product ovens, there would be an annual increased production of perhaps 375,000,000 gallons. That the development in this direction has been recently very strong is indicated by the fact that within the year ending in September new by-product ovens have begun operations turning out approximately 35,000,000 gallons of tar per annum.

QUALITY OF VARIOUS TARS

Depending upon the coal used, and more particularly upon the size and shape of retorts, the travel which the gases make over the hot surfaces, and the temperatures to which the gas is subjected, the coal tars vary within wide limits. In general with the vapors subjected to the higher temperatures usually characteristic of gas works as compared with coke works, there is an increase in specific gravity and free carbon. For example, the tar from many gas works will average about 1.24 specific gravity at 15.5° C. (60° F.) and about 25–30 per cent. free carbon by weight, whereas from the by-product coke ovens the specific gravity would average more nearly 1.19 and the free carbon would vary about 5–18 per cent., the average being less than 10 per cent.

The so-called free carbon represents a finely divided inert material, largely carbon, which is the portion of tar insoluble in benzol and toluol. Perhaps a very small part is carried over mechanically in the coking process, but for the most part it is due to the cracking of the hydrocarbons by exposure to heat, and the higher percentage usually found in gas works tars is from this cause. All gas works tar does not contain a high percentage of free carbon, as I found that in one of the largest European gas works the free carbon in the tar was only about 10 per cent., the percentage having been reduced very much from former figures by increase in the charging of the retorts and some other operating changes. There has recently been some development of the use of inclined and vertical gas retorts in the United

States, some of which produce tars lower in free carbon than many coke ovens.

The free carbon test of the various tars is very important because the percentage has a very considerable influence on the pitch product, and, moreover, it is an indication, to a certain extent, of the quality of oils and bitumens forming the balance of the tar. For many years there was very little coal tar produced in this country, except from gas works operating at very high heats, and the tar was extremely viscous, of high specific gravity and often containing from 30–40 per cent. free carbon. It was very difficult and expensive to distil such tar, because of the large percentage of water which is always contained and the tendency for excessive carbon to coke on the still bottoms and cause them to burn out. Because of this extreme, the lower carbon coke oven tars were welcomed as of relatively better quality, but to-day they are not necessarily more valuable as they yield pitches which are extremely subject to temperature influence—being very brittle when cold and easily flowing when heated—and therefore unsuitable for many pitch uses in the United States. The present vastly preponderating amount of very low carbon tars in many places is an extreme as unsatisfactory at times to the tar distiller as was the very high carbon gas tar. Much of the skill of the successful distiller is directed to a very careful study of the various tars he has to handle, the selection of each for the purpose for which it is best adapted, and the judicious combining of various tars to produce physical and chemical properties not possessed by any one of them separately.

The oil tars or water gas tars being largely produced from the petroleum oils used in making and enriching gas represents entirely different physical and chemical characteristics, containing compounds of the olefine series as compared with coal tar containing compounds of the aromatic series. In general they are much thinner and more oily than the coal tars, the specific gravity averaging about 1.07 at 15.5° C. (60° F.) and the free carbon about 1 per cent. The pitches produced from these tars, as might be expected, show, to a much higher degree, the properties of brittleness and susceptibility to temperature changes, and the oils have not given the very great value for timber preservation which is characteristic of the coal tar oils. For these reasons the water gas tars have been much less valuable commercially than coal tars and a large amount has been used as fuel. It is to be hoped and expected that further study will find special fields for the use of water gas tar and its products.

There are some small amounts of various other tars made, such as producer gas tar, lignite, wood tar, etc., but as yet these are not commercially significant, although some of them may develop considerably in the near future.

NUMBER AND LOCATION OF DISTILLING PLANTS

There are probably not more than about 40 tar distilling plants in the United States, most of them being naturally located near the producing sources in the section east of the Mississippi and north of the Ohio rivers. The tars will average to weigh about 9½ pounds per gallon and the freights from the gas or coke works are often 25–40 per cent. of the value of the tar at the shipping point, and for this reason there are many small distilling plants designed to take care of the output from only one or two local sources. At the same time there are large distilling plants in such cities as New York, Chicago, Philadelphia, Boston, Cleveland, Pittsburgh, St. Louis, etc.

TRANSPORTATION

Most of the tar in the United States is handled in steel tank cars of about 10,000 gallons (45 to 50 tons) capacity, such cars being largely owned by the distilling companies because of the need of specially designed equipment which the railroad companies do not furnish. These tank cars are of the usual horizontal cylindrical type, about 7 to 8 ft. in diameter and 28 to 30 ft. long, equipped with a dome on top and outlet valve in the

¹ Figured from data in chapter on "Coke," by E. W. Parker, "Mineral Resources of the United States, 1910."

bottom. As tar becomes very thick when cold, it is necessary to have an effective system of steam pipes for heating when unloading. The breakage of these coils—due largely to severe shocks in transportation—is a very troublesome and expensive experience. Where conditions permit, water transportation is used in harbor and sea-going barges from 25,000–300,000 gallons capacity or more. These boats are divided like oil boats into various compartments and equipped with steam coil systems and powerful pumps. In some cases the tar is handled through pipe lines from the producing plant to the distilling works, but long pipe lines, such as are used in handling petroleum oils, cannot be used with coal tar on account of the much higher viscosity of tar, especially when cold.

RECEIPT AT DISTILLING PLANTS

From the tank cars or boats, the tar is pumped (after being heated so as to render it more fluid) into storage tanks of varying sizes, generally from 250,000 to 2,000,000 gallons capacity. The large tar plants require many of these tanks so as to keep the various grades of tar separate, there being often four or five main grades and other special ones from time to time. These storage tanks are generally of steel bottom and sides, the roofs and roof supports being of wooden construction as steel roofs are subject to rapid corrosion. The wooden roofs are covered with built-up roofing of felt, pitch and slag or gravel. These tanks sometimes have steam coils covering the entire bottom, but more often only a small section around the outlet suction to permit warming the tar as rapidly as required to supply the pump. The tanks have small outlet cocks on the side distributed from the top to the bottom, so as to permit drawing off as far as practicable any water which was separated from the tar.

USES OF CRUDE TAR

Just as there existed a preference in favor of beehive coke, so for many years crude tar as received from the gas or coke works was preferred for some purposes, but a rational study has shown that the water and ammoniacal liquor contained in the tar are detrimental and only a small amount of tar is now being used in the crude state, except in such cases as the tar is used for fuel.

DEHYDRATION

It has long been recognized that one of the most troublesome and expensive steps in tar distillation is the removal of the water which is intimately mixed with the tar as received from the gas or coke works. The gas works tar is more troublesome because it contains a higher percentage of water, and at the same time the water is more difficult to remove because the tar is of greater viscosity and contains more free carbon. Many of the coke oven tars will average between 3 per cent. and 6 per cent. water, and the gas works tars between 4 per cent. and 10 per cent. water, although both kinds sometimes contain very much more, up to 40 per cent.

Two main facts to bear in mind explaining why the presence of water is so troublesome are: First, water at 100° C. (212° F.) when changing into steam increases in volume 1646 times, or in other words, a cubic inch of water becomes nearly a cubic foot of steam.

Second, water has the highest known specific heat. Dry tar has a specific heat of about 0.3 to 0.4, depending on the temperature and specific gravity. It will be noted, therefore, that it requires about three times as much heat to raise one pound of water 1° as it does one pound of dry tar.

Many methods have been used to dehydrate tar, perhaps the oldest one being that of allowing it to settle in storage tanks and depending on its lighter specific gravity to cause the water to rise to the surface. This process is aided by heating, intermittent heating with periods of settling being better than continuous heating. Steaming in large storage tanks is, however, very expensive on account of the great loss by radiation, and at best separates out only a portion of the water, particularly with gas

works tar. Other methods have been tried, such as centrifugal machines, squeezing the tar between heated rolls or in tanks under pressure, etc., but have not been commercially successful. The plan most in favor is that of heating the tar continuously in thin films under partial vacuum. This method ordinarily reduces the water to less than one-half of 1 per cent. Special dehydrator apparatus is in use at some of the large works having a capacity of about 50,000 gallons in twenty-four hours.

STILLS

After the tar has been dehydrated it is pumped to intermediate insulated storage tanks and thence as required to the stills for making the numerous grades of prepared or refined tars, soft, medium or hard pitches. Contrary to the German and English practice of using vertical stills with concave or convex bottoms, the still development in the United States has been mainly along the lines of horizontal cylinders. Quite a number of vertical stills have been used for particular conditions and have certain valuable characteristics. Many of the German stills up to recently held from 20 to 30 tons of tar, but the usual stills in the United States hold twice as much or more. One fact which is said to be largely responsible for the smaller unit abroad has been their desire to avoid night operation, whereas it is quite common with us. It seems quite probable to me that before very long we shall have in our large works in the United States three eight-hour shifts, with continuous running of the stills day and night, certain other portions of the works, however, operating only in the daytime.

Different types of brick still settings have been used with the general purpose of avoiding overheating and burning out the still bottoms and at the same time getting the maximum heat efficiency from the coal, liquid or gas fuel. Depending upon the local conditions and the quality of the oils and pitch desired, the stills are run with mechanical, steam or air agitation, or vacuum in addition to the usual heating. The temperature reached in the liquid in the still depends on the grade of pitch desired, the higher temperatures causing more oil to be distilled off and leaving a harder pitch, but the highest temperature does not usually exceed 400° C. (752° F.). The operation of these stills is intermittent, consisting of charging, distilling off the desired amount of oil, removing the residue by gravity, blowing or pumping, and repeating. Continuous stills have certain theoretical advantages, but have not been adopted in practice in the United States. Successful continuous distillation requires a uniform grade of tar and a demand for a very large amount of one grade of pitch for uses which permit quite a little latitude in range of melting point. Several continuous processes have been tried abroad, but have not met with general success; although I know of one very large plant where one continuous process is reported to have been operated with good satisfaction over several years at low cost. In many cases there has been too much fluctuation in the test of the pitch and oil product, but I feel sure the continuous process will come under conditions likely to develop in the future in this country.

OILS, CONDENSATION, USES, ETC.

The vapors escape from the still through a large vapor pipe to the condenser coils. All of the vapor pipe and preferably all of the coils should be made of flanged cast iron pipe using thin asbestos gaskets. In any case, it is necessary to use cast iron pipe as far as one or two turns below the water in the condenser tank, for the reason that certain of the vapors, particularly some of the ammonia compounds in the vapor form, attack wrought iron or steel very strongly, but have comparatively little action in the condensed liquid form. This is one reason why the tops of the stills sometimes eat through before the bottom. Most of the tars at present contain much less ammonia compounds than heretofore, as the ammonia is for obvious reasons recovered at the gas works or coke works.

The condenser tanks are usually square or oblong, with similarly shaped coils, the pipes ranging from six inches down to three inches. The length of the coil depends on the size of the still, the temperature of the available water, etc. The condensed oils are collected and measured in small steel tanks of about 100 to 400 gallons capacity, depending on the size of the stills and other conditions. These small tanks are provided with sight glasses and empty by gravity into a manifold pipe system leading to various large receiving tanks. From three to five fractions are usually collected, such as light oil, carbolic oil, middle oil, heavy oil and anthracene oil. The percentage of each fraction varies with the tars used and the commercial requirement for the oils, and no exact figures can be given. The total per cent. of oil secured in making pitch is generally from 20-50 per cent. by weight. From the receiving tanks the oils are pumped to large storage tanks for shipping or further refining.

The light oil, that having a specific gravity lighter than water, is separated from the water and then used as crude solvent in paints or for cleaning greasy gears, etc., or it is refined to benzol, toluol, solvent, naphtha, etc.

The carbolic fraction is usually collected so as to give the maximum yield of tar acids consistent with getting at the same time as liquid an oil as practicable. The carbolic oils, crude or redistilled, are cooled by natural or artificial refrigeration to remove excessive naphthalene and sold as crude carbolic acid for disinfectant manufacture. Inasmuch as from most tars the carbolic oils seldom contain more than 10-15 per cent. tar acids, and the usual standard required is 20-25 per cent., it is necessary to add extra acid as required. This is obtained by extracting the acids from other carbolic oils, or the middle and heavy oil fraction. The extraction process is a simple one of treating the oil under suitable temperature conditions with caustic soda solution, separating the sodium carbolate and throwing the acids out with sulfuric acid or more commonly with carbonic acid gas. The extracted acid is then redistilled and separated into carbolic acid and cresylic acid. The former is the basis for the purified crystal acid.

The demand for disinfectants is increasing with the campaign to reduce infectious growth and many excellent grades have been made for years, but at the same time many grades have been made unskillfully and are of no real value beyond the psychological one of having a good healthy odor. Just as a standard of purity or strength is required for foods, drugs, etc., it is reasonable to have a standard of efficiency for disinfectants, and the standard most widely recognized is the Rideal-Walker method of comparing with pure phenol under special conditions.

The large use for the middle, creosote and anthracene oils is for wood preserving, and they are fractioned so as to meet the various specifications of the wood preservers. This industry is a very large one and growing rapidly, as the conservationists have pointed out to large users of timber the definite fact that the local supply is gone and the more distant forests are being rapidly depleted. The railroads were among the first to appreciate the situation. Many of the large systems have had timber-preserving plants for years and now very few are without one or more of such plants. Other papers cover this creosoting industry, but in this connection it is of interest to note that the supply of creosote oil in the United States is much less than the demand, and the importations largely from England and Germany during the year 1911 were about 45,000,000 gallons.¹ This quantity represents, perhaps, about two-thirds of the total consumption. Recently there has been a very large increase in the use of creosoted wood blocks for paving as they make an ideal pavement under many conditions, particularly where a quiet pavement is desired in the business sections of large cities. Also there is an increasing demand for the higher distilling grades of creosote oil suitable for surface treatment of wood

(preferably by the hot and cold tank method), and high-grade domestic oils are now produced in large amounts.

Another use of creosote oils is for shingle stains, either plain or with colors. The use of certain fractions for Diesel and similar internal combustion engines in Germany has not developed here as yet because there are other more remunerative uses and in this special field there are various cheap petroleum products.

REFINED TARS AND PITCHES

Depending upon the amount of oil distilled off, we have as the residue in the stills either thick viscous tar or soft, medium or hard pitch. Sometimes the point for stopping distillation is determined by the still temperature or by the amount and test of the oil distillate, but such is possible only with a uniform grade of tar, and more generally samples are drawn from the still itself and tested, the distillation being continued until the desired grade is secured. The usual test is for melting point, which is determined by various arbitrary tests, as there is no such thing as a true melting point of a pitch. A general classification according to the half inch cube melting point would be as follows:

Distilled tars having a melting point less than 32° C. (90° F.).

Soft pitch having a melting point from 32° C. (90° F.) to 49° C. (120° F.).

Medium pitch having a melting point from 49° C. (120° F.) to 71° C. (160° F.).

Hard pitch having a melting point from 71° C. (160° F.) to 99° C. (210° F.).

Very hard pitch having a melting point from 99° C. (210° F.) upwards.

When the right grade has been secured the distillation is stopped and the still emptied either by blowing the contents direct from it by means of dry steam, or by drawing the contents by gravity to a special tank from which it is blown as before to storage tanks or coolers. From these the refined tar or pitch is later loaded into tank cars or tank wagons, or run into barrels, iron moulds or pitch bays, depending upon conditions.

Various grades of refined or prepared tars are made for road binders, for mixing tar concrete used under wooden floors in factories, for painting felt roofs and for saturating dry felt in making the various kinds of roofing paper. The grades are usually determined by specific gravity, distillation, free carbon viscosity, penetration, evaporation, etc.

The soft pitches are used for road binders, and alone or in combination with tarred felts for waterproofing the foundations of buildings, etc. In addition to the tests above, the so-called melting point is noted.

The medium pitches are very largely used for constructing "tar and gravel"—more properly "pitch and felt" roofs used on nearly all large factories having comparatively flat roofs. The construction consists of applying alternate layers of tarred felt and coal tar pitch, the laps or joints being broken and the top layer of pitch having embedded in it clean gravel or crushed slag. The standard construction to-day calls for at least five layers of felt besides the usual layers of pitch and gravel or slag. Other large and growing uses are that of paving pitch for filling the joints of brick, stone and granite pavements, and for waterproofing bridges, etc. These grades of pitch are usually shipped in barrels.

The hard pitches are most largely used for briquetting coal dust or slack. This promises to become a very large industry in the United States later on when lump coal is more expensive, and has already become well established in certain sections where briquettes are made from anthracite dust for domestic use.

The very hard pitches are used for electric carbons and batteries, for insulating, for making "clay pigeons" or "flying black-birds" used for target shooting, for making core compound used in foundries. These pitches are so hard that they can be ground to powder. The hard pitches are run hot either into iron moulds

¹ House of Representatives Report No. 326, p. 65.

or into pitch bays or pits and there allowed to cool. The iron molds can be emptied when cold and the pitch can be dug or mined from the bays and is handled to cars for shipment. Most of these hard grades are shipped in bulk so as to save packages and the freight on same.

ROOFING PAPER

One important branch of the tar industry is the manufacture of roofing felts, largely a mechanical process and therefore one in which we are further advanced here than abroad. The felt forming the basis of these roofings is made from mixed old woolen and cotton rags, largely cotton, along the lines similar to other paper manufacture. Various widths are used, generally thirty-two inches or thirty-six inches, and the paper varies in thickness from the No. 15 to the No. 80 of the paper-maker's scale, weighing from 3.1 to 16.7 pounds per one hundred square ft., single thickness. This felt is made in large rolls weighing about 400 to 600 pounds.

The simplest form of manufacture is the saturation of such felt by passing the sheet continuously through a bath of refined tar, then through revolving squeeze rolls, which remove the surplus tar, and the tarred felt is wound into measured rolls often containing 400 to 500 square ft. This kind of tarred felt is largely used in the "felt and pitch" roofs and also for waterproofing and sheathing purposes.

The so-called prepared or ready-to-lay roofings are of many different kinds, one standard form consisting of two or three layers of tarred felt cemented together with pitch and having a plain surface or one covered with pitch or composition into which, while hot, is embedded crushed feldspar or small pebbles.

REFINED PRODUCTS

The refined products, as noted above, are largely of the general benzol, naphthalene, anthracene group. Much more crude benzol is now obtained by washing coke oven gas in oil scrubbers than is obtained from coal tar distillation. This gas oil or the light oil from distillation is redistilled, treated with sulfuric acid, washed, treated with soda and then distilled with steam. Fractions are collected distilling within certain limits, such as pure benzol, 90 per cent. benzol, toluol, xylol, etc. These are very largely used in this country as solvents, especially in paint and varnish lines, for making varnish remover and as a basis for nitrobenzol, aniline, etc.

Crude naphthalene is purified by crystallizing, passing through centrifugals to remove the oily portions, distilling, treating with sulfuric acid and crystallizing or subliming.

Large amounts are used for moth balls. Specially purified naphthalene is the raw material for making many coal tar colors, this line being hardly touched in the United States, for reasons noted above. Recently some new wax products have been introduced having peculiar dielectric properties, and promise to develop an important field. These are made from naphthalene by a chlorination process.

Anthracene as the basis for alizarine was of great importance at one time, but is not largely purified at present because of the low market price.

Although brilliant chemists have been studying tar products for years, yet the number of constituents and the innumerable combinations which can be produced by treating them with other compounds leaves plenty of opportunity for the future. The recent opening up of various pressure, electrolytic and catalytic processes will probably give us more astonishing products from tar than any yet secured, each success stimulating the world of scientists to further efforts. That the United States will ultimately take a prominent position in the industry is to be expected from the future great supply of tar in this country, and the energy of her students who admire the success of the German, English, French and Swiss chemists and are determined,

if possible, to go one or more steps further. Fortunately there is ample room for all in this fascinating line of work.

NEW YORK CITY

DISPOSAL OF SEWAGE WITH RECOVERY OF ELEMENTS OF PLANT FOOD FOR USE IN AGRICULTURE

By WILLIAM McMURTRIE

Received October 9, 1912

The hygienic disposal of the excremental dejecta of the human population of cities has long been a difficult and troublesome problem, and the best minds of the engineering, chemical and biological professions have been taxed in its solution. It is the purpose of this paper to treat the subject from the chemical standpoint and to call attention to means whereby the organic and other constituents of excremental dejecta of value for plant food may be, in some measure at least, removed from sewage and recovered for use in agriculture.

The desirability of some method whereby this may be satisfactorily and economically accomplished has long been acknowledged and much work has been done with this end in view, but thus far the results have not been altogether encouraging. The importance of recovering the elements of plant food from this source has been recognized by many of the great economists of the world and much thought, effort and means have been devoted to it. In his memorable address to the Bristol meeting of the British Association for the Advancement of Science in 1898 Professor William Crookes said: "There is still another and valuable source of fixed nitrogen. I mean the treasure locked up in the sewage and drainage of our towns. Individually the amount lost is trifling, but multiply it by the number of inhabitants and we have the startling fact that in the United Kingdom we are content to hurry down our drains and water courses and into the sea, fixed nitrogen to the value of no less than 16,000 pounds sterling per annum. This unspeakable waste continues and no effective and universal method is yet contrived for converting sewage into corn. Of this barbaric waste of manurial constituents Liebig, nearly half a century ago, wrote in these prophetic words: 'Nothing will more certainly consummate the ruin of England than a scarcity of fertilizer; it means a scarcity of food. It is impossible that such a sinful violation of the laws of nature should forever remain unpunished; and the time will probably come for England sooner than for any other country, when, with all her wealth in gold, iron and coal, she will be unable to buy one-thousandth part of the food which she has, during hundreds of years, thrown recklessly away.' "

What Professor Crookes has so ably said regarding Great Britain is equally true of the other countries of the world. It would be an interesting study to work out the relation between the fall of the Roman Empire, and the sterilization by continued and consecutive cropping of the wheat fields of the great Campagna and other parts of Italy, the impoverishment of Greece, Turkey and Syria and the wasteful and unintelligent use of the great sources of their supplies of food and clothing, and at the same time to work out the relation of the prosperity of the modern nations to the intelligent management of their agricultural resources. While the people of the United States are earnestly considering, as a nation, the conservation of natural resources it would seem equally important to give no less attention to the conservation and utilization of the wastes, not only of the cities but also of the farms and forests. It would be a study of fascinating interest and well worthy of the thought and effort of our statesmen and economists. Reference has frequently been made in the economic literature to the practice in China of gathering scrupulously all human excreta for use on the farms, and the consequent maintenance of the fertility of the soil for centuries. It behooves us of the professedly more civilized nations, to take some lessons from our neighbors

across the Pacific and utilize our wastes as they have theirs.

While it is possible that the estimate of Professor Crookes is fairly generous it is quite likely that in his estimate, he applied the available data regarding human excreta—including both feces and urine—to the entire population of the United Kingdom and not simply to the urban population connected with sewage systems. It must be borne in mind that the sewages of England and of the European continent are considerably more concentrated than are those of the United States. In considering the waste carried off in sewage the data should be applied to urban population alone. If the excreta of the rural population are wasted it is the fault of the producers. Estimates similar to that offered by Professor Crookes made for the United States and based upon data from various sources are not as striking as those given by the eminent English scientist but they are both impressive and interesting. According to the last census the urban population of the United States in 1910 was 42,623,383, and at the present time must be approximately 44,000,000. To arrive at a reliable conclusion regarding the manurial value of the excreta of this great population, as great as that of the whole of either England or Germany, is not easy because of the lack of reliable determination and records of the amounts of excreta produced and the composition of the product.

Perhaps no authority has given closer attention to the disposal of sewage than Ferdinand Fischer, the eminent German technologist of Göttingen. According to this authority the weights of feces and urine and the contained nitrogen and phosphates from one thousand persons amount annually to

	Feces Quantity Kilograms	Urine Quantity Kilograms
Total weight.....	33,166	428,190
Contained nitrogen.....	489	3,482
Contained phosphate.....	687	1,725

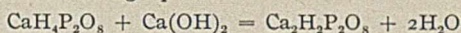
If we accept these figures as representative of the quantity and composition of the fecal excreta of the urban population of the United States the results are interesting. For we may consider that the citizens of the United States are at least as well fed as those of Germany and the quantity of excreta produced should, therefore, be no lower. On this basis we must conclude that the 44,000,000 urban population of the country produces annually dry fecal matter containing over forty-seven million pounds of nitrogen which at 15 cents per pound represents a value of over seven million dollars. This, of course, takes no account of the phosphoric acid which should also be recovered in the process we are about to suggest. If we add to the above figures those for phosphoric acid in feces and urine, which would also be recovered by the process in question, we have an additional total per annum of \$8,800,000. This makes a grand total value of almost sixteen million dollars for the plant food annually recoverable from the urban sewage of the United States. According to another eminent German authority, Heiden, quoted by Storrs in his work on agriculture, the nitrogen voided in human feces amounts per annum to 1.7 pounds per capita, and the phosphoric acid voided in both feces and urine amounts to 2.6 pounds per capita. On this basis the figures named would be even higher.

Yet the figures we have given, based upon data from different sources, are reasonably correct and may, we think, be accepted as fairly representative of what may be expected from the careful and intelligent treatment of the sewage of the United States. In view of the importance of the conservation of our resources it would seem eminently desirable that means should be adopted for the conservation of this source of wealth otherwise destroyed and lost.

We come then to the method proposed for the removal of the suspended matter of urban sewage and its recovery for use in agriculture. Many methods have been proposed and applied, from broad irrigation and plain sedimentation, to the various

methods of chemical precipitation. Much prejudice has been expressed against chemical precipitation because of inefficiency of clarification, the interference of excess of precipitants with the septic purification of the effluent, and the slight value of the sludge for use in agriculture. All this indicates that care must be exercised in the application of any precipitant. Aluminum sulfate so largely used, when used alone is effective only in very hard waters whose hardness is due to the presence of carbonates, yet it has been frequently used in sewages resulting from the consumption of waters practically free from hardness. Ferrous sulfate has been extensively employed in conjunction with lime, the ferrous hydroxide formed serving as the coagulant to precipitate the suspended matter, but it frequently happens that in order to preliminarily dry the sludge by removal of liquid water in the filter press, excess of lime is used to the extent that a large portion, at least, of the nitrogen is expelled in the form of ammonia, the agricultural value of the sludge is consequently reduced, and the operation of clarification made very offensive.

The precipitant here recommended is acid calcium phosphate ($\text{CaH}_4\text{P}_2\text{O}_8$), commercially known as superphosphate of lime, in conjunction with lime. The acid calcium phosphate (produced by the action of sulfuric acid on tri-calcium phosphate) which may be used as such or in admixture with free phosphoric acid is added to the sewage and thoroughly mixed with it. When the admixture is complete and the solution is homogeneous, lime in the form of milk of lime, $\text{Ca}(\text{OH})_2$, is slowly added, with simultaneous vigorous agitation of the liquid, in quantity sufficient to meet the demands of the reaction indicated in the following equations:



and in order that the carbonic acid may be removed at the same time and so have no interfering action on the formation of di-calcium phosphate, enough lime must likewise be added to combine with the carbon dioxide in the liquid. Thus:



that is, soluble acid calcium phosphate is converted into di-calcium phosphate which, at first, is flocculent and encloses all suspended particles; and subsequently becoming crystalline, particularly in consequence of violent agitation of the liquid, remains attached to the solid particles and rapidly carries them down in sedimentation. After precipitation has been completed the sewage is allowed to flow into sedimentation cisterns or is transferred to Dortmund tanks. If the Dortmund tank with conical bottom is used it should be so proportioned that the upward flow will not exceed 0.02 inch per second. The sludge which settles into the cone may be drawn off from the bottom to the filter press or centrifugal and when partially dried by this means it is sent to cylindrical direct-heat rotary driers, where it is dried to the commercially allowable 10 per cent. of moisture.

But the calcium phosphate does more than carry out the solid suspended matters. It combines by adsorption with the apparently soluble colloidal matter and carries it down as well, wholly or in part, and hence carries down a very large portion of the bacteria, making a clear colorless nearly-bacteria-free effluent. The effluent is in excellent condition for further treatment by sand filtration, intermittent filtration or any of the biological means which have been suggested for the treatment of sewage, raw or settled. The removal of the colloidal matters in addition to the suspended matter so purifies the sewage that generally it may be discharged into any considerable body of water or stream of reasonable volume without deleterious result.

The Dortmund tank offers the advantage that it may be installed upon a smaller area than that consumed by the tanks or cisterns of the septic system, a very important consideration when it is desired to establish a purification or disposal plant

within the confines of a municipality. With the Dortmund tank, or the Machlachlan tank, which is very similar, the treatment of a large body of sewage may be effected in a comparatively small space.

The use of phosphate has this advantage over aluminum or iron salts: that the precipitate of the former does not remain flocculent but becomes crystalline and that sedimentation is thereby promoted and is more prompt and rapid. In addition to this the phosphate precipitate has an agricultural value as plant food which, of course, the aluminum and iron precipitates do not have. Furthermore, the use of an excess of the precipitant, while unwise, can have no deleterious influence upon the agricultural value of the sludge and in case excess is accidentally used the phosphate will be recovered in the sludge and no ultimate loss occasioned. Yet the quantity of phosphate used should be such that the precipitated phosphate should have nearly the same weight as the suspended solids. This is essential to the best results in precipitation and in draining the sludge.

The settled sludge obtained varies in its properties in accordance with the quantity of phosphate used in producing it, and the mode of application of lime to the sewage as well as the completeness with which carbonic acid has been simultaneously precipitated. If the lime be added too rapidly there will be tendency to production of tri-calcium phosphate which will remain permanently flocculent and so interfere with filtration. Furthermore, it is not so readily soluble in the soil and has a somewhat lower agricultural value than the di-calcium phosphate. In the absence of carbonic acid di-calcium phosphate is insoluble in water and all the phosphate used, if care is exercised, may be completely recovered and in form practically as valuable for plant food as the acid calcium phosphate originally employed. In addition to the nitrogen of the suspended matter the phosphate contained therein as well as much of the phosphate contributed to the sewage by urine is secured. It has been found that one million gallons of sewage will return at least half a ton of dry sludge and in some cases more than this. The sludge contains about 1.5 per cent. of nitrogen and depending upon the amount of phosphate used in the precipitation, over twenty per cent. of phosphoric acid. The value of the sludge independent of the amount of phosphate employed will be from four to five dollars per ton on account of the nitrogen recovered, and while the material recovered cannot be expected to cover the cost of recovery or treatment of the crude sewage it contributes materially toward the net cost of disposal. Thus if the cost of disposal, by the septic or biologic process, amounts to five dollars per million gallons which will probably not be considered too high an estimate, the cost of precipitation with the phosphate will not greatly exceed this and the returns from nitrogen recovered will very nearly balance the account. We not only provide here a means for purifying the sewage to the extent that it may be discharged without further treatment into most of the water courses without offense, but the material recovered partly covers the expense of treatment. Besides this we have provided for the conservation of the very important urban waste for use in agriculture.

The process may be equally well applied to the treatment of turbid and colored water supplies. Suspended matter is completely removed, and the coloring matters, particularly when plenty, are coagulated and precipitated furnishing an effluent clear, colorless, and with bacterial content very materially reduced, generally to an extent entirely allowable in good potable water. In addition if the precipitation be affected by sodium carbonate followed by lime the hardening constituents will be simultaneously removed and the water consequently softened.

The process has not yet found extended application but enough has been done with it to prove its availability for the successful treatment of municipal sewage, and the recovery

by means of it of the suspended organic and much of the soluble phosphates present therein.

It is important that the process shall be operated in careful and skilled hands. If carbonic acid is not removed, di-calcium phosphate is not as well precipitated and a considerable loss may be occasioned. If the lime is added too suddenly and in too large quantity at a time the tendency to the formation of tri-calcium phosphate will interfere with prompt and rapid sedimentation and will increase the cost of recovery as well as reduce the value of the sludge.

If too much lime is used, more than is necessary to precipitate the phosphoric acid added and the urine phosphoric acid present, as di-calcium phosphate and carbonic acid as calcium carbonate, making a neutral effluent and sludge, there will be liberation of ammonia with consequent loss of nitrogen and production of offensive odors. If violent agitation is not provided when the lime is being slowly added, crystallization is not so prompt and sedimentation not so rapid.

The sludge, if sufficient phosphate has been used in the precipitation, and proper agitation of the sewage has been applied during precipitation, should be capable of being drained of mechanical or liquid water in a filter press or even upon a gravity filter, and then the character of the sludge is such that it is too viscous and colloidal to admit of successful treatment in the filter press or on the gravity filter, then it may be treated in one of the several centrifugal machines designed for the purpose.

The sludge dried by means of the filter press or the centrifugal may be further dried at very small cost in any one of the direct-heat cylindrical rotary driers, and bagged for storage, transportation and use.

The process is well worthy of the considerate attention of engineers charged with the disposition of the municipal sewage. It would seem a public duty to use every means to conserve the municipal waste caused by the method ordinarily employed for the treatment of sewage. Among the advantages of the process may be named:

1. The precipitation of the suspended matter is complete.
2. The effluent is clear, colorless, and has comparatively low bacterial content.
3. The effluent may be discharged into water courses without further treatment and without serious detriment, particularly if treated with calcium hypochlorite or other disinfecting agent.
4. The organic suspended matter and much if not all of the colloidal matter in the sewage are recovered in condition suitable for use in agriculture.
5. The phosphate employed is recovered in form available directly as plant food, and therefore of as high value as that originally employed. The cost of the phosphate beyond a small mechanical loss in handling and interest upon funds invested in the product may be disregarded.
6. It is probable that much of the phosphoric acid furnished to the sewage by urine will be recovered in the sludge.
7. The net cost of the disposal of sewage will be materially reduced.
8. In this process, sedimentation is more rapid than in ordinary sedimentation processes and may be effected in the Dortmund or Machlachlan tank.
9. The space required for the plant and the expense of constructing the plant are considerably less than like items for septic or biologic plants which are so extensively used. The plant may, therefore, be installed within city limits, where, because of the space required, the other processes named would be wholly impracticable.

The disadvantages of the process, if there are any, will quickly be discovered. Among these may be mentioned:

1. The difficulty of separating the mechanical or liquid water from the sludge. If the lime has been added too rapidly or much colloidal matter is present in the sewage, filtration is slow

2. The necessity for daily care of the sludge and the labor involved in it.

The advantages of the process, however, seem to outweigh the disadvantages by an adequate margin, and the process is, therefore, commended to the favorable consideration of engineers and chemists charged with the disposal of municipal sewage.

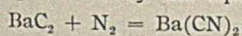
264 RIVERSIDE DRIVE
NEW YORK CITY

MANUFACTURE AND USES OF CYANAMID¹

By E. J. PRANKE

The problem of the fixation of atmospheric nitrogen is one which has engaged the attention of scientists for the greater part of a century. The rapid growth of the fertilizer industry that has attended the development of agricultural science, and the great increase in the number and extent of chemical industries, during the past fifty years, has emphasized the necessity for artificial methods of maintaining and increasing the world's stock of combined nitrogen. One of the influences that stimulated immediate action was the introduction in 1887 by MacArthur and Forest, and at about the same time independently by Siemens and Halske, of Berlin, of the Cyanide Process for leaching gold and silver from their ores. This produced a strong demand for cyanides, which had hitherto been used to the extent of only a few hundred tons a year, principally in the dye industry and to a smaller extent in electroplating.

Attempts had been made early in the nineteenth century to bring about the direct synthesis of cyanogen from atmospheric nitrogen and carbon. Among other processes, that worked out in 1847 by Bunsen and Playfair, in which barium carbonate was heated in an atmosphere of pure nitrogen, seemed promising, but did not prove to be commercially successful. The introduction of the electric furnace in 1894 by Moissan and by Willson, for the production of carbides on a large scale, gave new direction to the researches. Siemens & Halske, among others, adopted it for the working out of the problem of nitrogen fixation. In 1895 they worked on the process of Prof. H. Mehner, which consisted in fusing a mixture of sodium carbonate and carbon and conducting nitrogen through the hot mass. In the same year they took up the process of Prof. Adolph Frank and Dr. Nicodem Caro, which consisted in subjecting a mixture of barium carbide, sodium hydroxide, potassium hydroxide and carbon at a high temperature to the action of steam and nitrogen. Frank and Caro, with the coöperation of F. Rothe, soon learned that dry nitrogen is essential to successful absorption. In 1898 it was found that barium carbide alone, heated to a temperature of 700 to 800° Centigrade, in an atmosphere of nitrogen, readily absorbs nitrogen and forms a product in which about 30 per cent. of the nitrogen is present as barium cyanide and about 70 per cent. as barium cyanamide. The reactions may be represented by the equations:



It was further found that on fusion of this mass with soda the cyanamide is converted to cyanide. This mass can then be leached with water, and the cyanide solution thus obtained can be converted to sodium ferrocyanide, which is easily separated in a pure form, and which can be sold as such or be converted into pure sodium cyanide by fusion with metallic sodium.

The interruption in the production of gold in Africa, due to the Boer war, caused a decline in the price of cyanide, which stimulated the search for cheaper methods of production. It was found that calcium carbide could not only be manufactured at a lower cost, but it had the advantage of a lower molecular weight. With calcium carbide a temperature of from 1100 to 1200° C. is required for absorption, but in this case the nitrogen

¹ Address before the Nashville Section of the American Chemical Society, November 15, 1912.

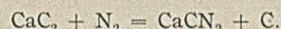
is fixed exclusively in the form of calcium cyanamide. On fusion with alkaline salts the cyanamide is readily converted to cyanide, and this can be extracted and purified in the usual manner.

Agricultural experiments with the crude calcium cyanamide showed that this material is suitable for use as a nitrogenous fertilizer, and patents were issued in 1910 to Dr. Albert R. Frank, son of Prof. Adolph Frank, and to Herman Freudenberg, a co-worker of A. R. Frank, protecting the use of Cyanamid for this purpose. The basic patent protecting the process of manufacture of Cyanamid was issued to Prof. Dr. Adolph Frank and Dr. Nicodem Caro in 1908.

The large demands of agriculture for cheap nitrogenous fertilizer materials have directed the efforts of the manufacturers towards the production of Cyanamid rather than of cyanides and other derivatives. At present the total output of sodium cyanide derived from Cyanamid is only about 2000 tons per annum, while the world's production of Cyanamid is estimated at about 120,000 tons per annum.

MANUFACTURE OF CYANAMID

Calcium cyanamide is formed in accordance with the equation



The raw materials, therefore, are calcium carbide and nitrogen. Calcium carbide is formed in accordance with the equation



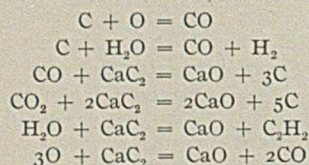
The raw materials for this reaction, therefore, are lime and coke.

For the production of carbide, lime, from 1 inch to 2½ inches in size, and coke, about ½ inch, are mixed, in the proportions demanded by the equation, to produce a carbide about 80 per cent. pure. The mixture is shoveled continuously into a 3-phase electric furnace. The furnace consists of a supporting base and four retaining brick walls which are filled with the lime and coke mixture, into which is submerged three carbon electrodes carrying the current. The resistance of the materials to the passage of the current raises them to a temperature at which the lime melts freely and combines with the coke to form liquid carbide. At intervals, as the carbide accumulates, it is tapped off through a suitable tapping hole at the side of the furnace into iron cars. After cooling, the carbide is crushed and ground to a fine powder, and is then packed in perforated cylindrical steel cans in the axis of which is a cylindrical paper core. The can with the carbide is set in a brick walled oven, slightly larger than the can, and is covered with an iron lid. A carbon pencil is run through the paper core in the axis of the can. Upon passage of the electric current, the carbide is heated, nitrogen is admitted to the can, and the absorption takes place very readily, raising the temperature to about 1100° to 1200° C., at which point it is maintained until the absorption is complete. The reaction $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ is exothermic, and the heat given out is almost sufficient to maintain the mass at the combining temperature. Upon completion of the reaction the cans are removed and the product is allowed to cool. It is a bluish black solid, containing small glistening crystals of pure calcium cyanamide.

PREPARATION

The nitrogen required for the manufacture of Cyanamid is separated from the air by either the liquid air process or the copper oxide process. The latter is in use at present by the American Cyanamid Company. The copper oxide process is based upon the ease with which heated copper combines with oxygen. The very finely divided copper suspended in a mass of asbestos or other inert material is contained in boiler shells provided with means for supplying heat externally. Air is pumped through the retort, which is at about 800° C., and is completely deprived of its oxygen. The nitrogen is then freed from carbon dioxide by passage through a caustic soda tower. The moisture

is removed by refrigeration, followed by passage of the gas through layers of lime, and finally through calcium chloride. The nitrogen must be pure and dry, since otherwise there is a destruction in the nitrifying ovens of the carbon pencil and of calcium carbide in accordance with the following reactions:



The oxidized copper in the nitrogen separation retorts is reduced in place by reducing gases, such as natural gas.

PREPARATION FOR USE AS A FERTILIZER MATERIAL

The crude Cyanamid obtained from the nitrifying ovens, after cooling, is crushed to a fine powder, and is passed into rotating, slightly inclined, steel cylinders, in which it is treated with sufficient water to eliminate the carbide and to slake the calcium oxide. A further slight addition of water is made before the material is run through briquetting machines.

The resulting bricks harden rapidly and are stored until they can be crushed just prior to shipment. Crushing is done in a series of rolls with intermediate screens, the final product having a coarseness of about 15- to 50-mesh screens. It is packed in ordinary fertilizer bags and distributed in carload lots to manufacturers of mixed fertilizers. The material so prepared contains nitrogen equivalent to about 19 per cent. ammonia.

It analyses approximately as follows:

Calcium Cyanamide	45%	Iron and Alumina	2%
Calcium Carbonate	4%	Silica	2%
Calcium Hydroxide	27%	Combined water	4%
Calcium Sulphide	1%	Free moisture	1%
Free Carbon	14%		

USES OF CYANAMID

At present, Cyanamid is used in this country principally for agricultural purposes. It is known to have a fertilizing value equal or superior to that of other common products used for the same purpose. Some of the earlier experiments with this material indicated an uncertain action on very acid moor soils, but the same thing is true of other fertilizers requiring nitrification prior to absorption by the plant, and is the fault of the soil and not of the fertilizer. Such soils must be restored to normal condition before fertilizers can be expected to have their full effect. In other cases, experimenters applied quantities far in excess of those used in practical agriculture, and obtained a lower efficiency of utilization than with the normal applications. As a general conclusion from the hundreds of recorded experiments and from the testimony of practical agriculturists, it may be said that when Cyanamid is used in the same way as other fertilizers are used in ordinary practice, its efficiency of utilization is about the same as that of the high-grade fertilizer materials, and superior to that of the low-grade fertilizer materials.

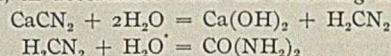
The particular advantage of Cyanamid as a fertilizer material lies in the advantageous effects that follow its admixture with other constituents of complete fertilizers. It greatly improves the mechanical condition of such mixtures, and by its alkaline properties prevents the escape of valuable nitrogen oxides and of bag-rotting hydrochloric acid, set free by the action of free acids in acid phosphate upon nitrates and chlorides in the mixtures.

Statements have been made that there is a loss of ammonia from Cyanamid during long-continued storage. It has been found, indeed, that the nitrogen percentage in stored material does decrease, especially in very damp climates, but it has been determined by very careful experiments both on a small scale and on a large scale in fertilizer factories, that such decrease in

the nitrogen percentage is due not to any actual loss of nitrogen, but to the increase in the weight of the material, due to its absorption of carbon dioxide and of moisture from the atmosphere. Part of the moisture absorbed is fixed chemically into forms from which it is not recovered on heating in a drying oven, hence it is necessary, when testing the storing qualities of this fertilizer, to weigh the material before and after the period of exposure and to determine the nitrogen percentage each time.

SOIL ACTION OF CYANAMID

It has been definitely established by the researches of Ulpiani and Kappen, among others, that cyanamid applied to the soil is completely converted in the course of a few days into urea, by the catalytic action of the colloids and other constituents of the soil, in accordance with the following reactions:



The urea is further converted by bacterial action and possibly by chemical processes into ammonia, which further reacts with zeolites, humates, and other soil constituents, to form double ammonium salts, that are retained as a part of the soil, until further bacterial action or the solvent effect of plant roots makes them available to vegetation. Cyanamid is said to be completely utilized by the crop in from 60 to 80 days.

OTHER USES

When Cyanamid is subjected to the action of superheated steam under pressure of several atmospheres, it is converted almost quantitatively into ammonia and calcium hydroxide. It thus serves as a convenient and cheap source of pure ammonia. By the Ostwald process, which uses thoria and ceria as catalytic agents, ammonia can be commercially converted into nitric acid.

By fusion of Cyanamid with alkaline salts in the presence of carbon, cyanides are easily produced and can be separated and purified as desired.

When Cyanamid is extracted with water between 70° and 100° C., nearly all of the nitrogen is converted into dicyandiamide (H_2CN_2)₂. This compound is used in the dye industry and also in the explosives industry in place of ammonium oxalate to reduce the temperature of the explosive gases.

Other derivatives, such as urea, guanidin and its salts, and various dicyandiamidin salts are now being manufactured in Germany. One or both of the hydrogen atoms in the amide group in cyanamide, CN.NH_2 , can be replaced by metals, alkyl or aryl groups, alcohol groups, aldehyde groups, and others, thus leading to an immense number of organic derivatives. The possibilities in this field have been investigated but little.

Various compounds of Cyanamid, and its derivatives, with alkaline salts and carbonaceous materials, are made and sold in Germany under the names of Ferrodur, Intensit, Hessolin, and others. These compounds, known as "hardening" or "cementing" powders, are used in place of cyanides, ferrocyanides, waste leather and similar materials, for case-hardening of steels. These products containing Cyanamid are not only cheap but they are efficient for the purposes for which they are intended.

FUTURE OF CYANAMID INDUSTRY

The Cyanamid industry is undoubtedly only in its infancy. At present there are four factories in Germany, four in Italy, two in France, and one each in Austria, Norway, Sweden, Switzerland, Japan, and America. The American Cyanamid Company built its first plant at Niagara Falls, Ontario, in 1909, beginning commercial manufacturing January 1st, 1910. Additions to the plant, which will be completed in March, 1913, will give a capacity of 25,000 tons per annum, and by the end of the year the full productive capacity of the company, including the extensions now under way, should be 50,000 tons per annum.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

UNITED STATES STATISTICS FOR 1912

Number 2 of Volume 95 of *The Engineering and Mining Journal* contains a comprehensive treatment of many of the minor and major minerals and metals, giving statistics of production for 1912, and reviewing progress in various departments of metallurgy. An abstract of this entire number follows.

PRODUCTION OF METALS IN THE UNITED STATES IN 1912

METAL	UNIT	PRODUCTION
Copper ¹	Pounds	1,242,836,024
Ferromanganese	Long tons	202,186
Gold ²	Dollars	91,685,168
Iron	Long tons	29,445,068
Lead ³	Short tons	418,224
Nickel ⁴	Pounds	33,311,233
Mercury	Flasks (75 pounds)	25,147 ⁵
Silver ²	Troy ounces	62,369,901
Zinc ⁶	Short tons	347,922

¹ From ore originating in the U. S.

² Preliminary statistics reported by Director of Mint..

³ Refined lead from ore and scrap originating in the U. S. Antimonial lead included.

⁴ Imports for first 10 months of 1912. This nickel is refined in the U. S. for the production of metal, oxide, and salts.

⁵ Reported by U. S. Geological Survey.

⁶ Total production of smelters, except those treating dross and junk exclusively; includes spelter derived from imported ore.

MINERAL AND CHEMICAL PRODUCTION OF THE UNITED STATES IN 1912

SUBSTANCE	UNIT	PRODUCTION
Arsenic	Pounds	5,852,000
Coal, anthracite ¹	Short tons	511,964,403
Coal, bituminous ¹	Short tons	427,655,966
Coke ¹	Short tons	41,803,199
Copper sulfate	Pounds	39,480,741
Iron ore	Long tons	59,485,477
Petroleum	Barrels (42 gallons)	218,970,815
Tungsten ore	Short tons	1,290 ²

¹ Estimates of *Coal Age*.

² Reported by U. S. Geological Survey.

METAL PRODUCTION OF THE WORLD IN 1912

METAL	UNIT	PRODUCTION
Gold ¹	Dollars	469,618,083
Silver ²	Fine ounces	229,569,903
Copper ³	Metric tons	1,004,844
Tin ⁴	Long tons	114,196
Platinum ⁵	Ounces	322,000

¹ The Transvaal furnished 40.1 per cent. of the total, the United States supplied 19.5 per cent., and Australasia 12.1 per cent.

² London continues to be the chief silver market of the world. Mexico is the largest producer, having contributed 76,500,000 fine ounces in 1912; the production of Canada was 35,250,000 fine ounces in 1912.

³ Figures are based upon crude copper, i. e., the smelters' production. The United States supplies over half of the world's production.

⁴ The visible stocks of tin on December 31, 1912, were reported to be 10,977 long tons. The average price during the year was 46.096 cents per pound as against 42.281 cents in 1911.

⁵ Includes productions of Russia (310,000 ounces) and Colombia (12,000 ounces). Small quantities are also obtained in British Columbia and Australia, but the amount is unimportant.

There were 60,178,477 tons of iron ore consumed in the United States in 1912, and the production of pig iron amounted to 29,647,274 tons. The following table shows the production for 1912 classified according to the uses for which it was intended:

Foundry and forge.....	5,965,591
Bessemer.....	11,740,055
Basic.....	11,386,176
Charcoal.....	353,266
Spiegel and Ferro.....	202,186

Total..... 29,647,274 tons

The sulfur industry in 1912 was marked by new activities

in exploration. The Union Sulfur Co. produced in 1912 more sulfur than the entire world consumed. No Sicilian crude was imported in 1912, although a few thousand tons of refined sulfur came from that source, and probably about the normal amount was imported from Japan at Pacific ports. A quiet year was experienced by the importers of pyrites; the domestic mines supplied about 300,000 tons, or less than 25 per cent. of the normal consumption of the United States, but, due to the over-extension of the phosphate industry in 1911, the 1912 demand was light.

THE CHEMICAL ACTIVITIES OF BELGIUM

There are 10 zinc works, producing 48,450 metric tons of finished zinc, and 13 zinc foundries, producing 198,230 metric tons of rough zinc, in operation in Belgium. In the Province of Hainaut there were 2,057 coke ovens in operation in 1911, consuming 2,698,480 metric tons of coal. Other statistics for 1911 follow:

PRODUCT	IMPORTS	EXPORTS
Chemical products	\$24,646,197	\$14,587,631
Window glass	75,576	7,163,165
Plate glass	49,022	5,643,952
Iron and steel	18,332,894	1,624,562

THE INCREASED USE OF CHARCOAL IRON

Some very good work (A. I. Findley, *The Foundry*, 40, 534) has been done recently in the direction of giving charcoal iron a larger place in car wheel and special mixtures. There have been some results, and the demand upon the railroads for freight car wheels which will better stand the heavy service of recent years is assisting the movement. However, cost is so controlling an influence in railroad buying that the low level of coke pig iron has held down the charcoal product, and much is yet to be done to secure recognition for it on the score of quality. In chilled work and for castings requiring a special selection of raw material, charcoal iron is making headway, and the outlook has been sufficiently promising to encourage some additions to the capacity of Michigan charcoal furnaces in the past three years. Lately, Mayari pig iron, which owes its properties to a small content of nickel and chromium, has been offered as a component of chilled roll mixtures and for castings requiring special strength.

A new process for making charcoal wrought iron is being operated by a works near Philadelphia, Pa. An open hearth furnace is used; it is first heated by oil or gas, and then a layer of charcoal is spread on the hearth and the charge of pig iron is placed on top of it. The iron is covered with a layer of charcoal, then cold air from tuyères burns the charcoal, melts and boils the iron in the customary manner. The fused metal runs through the lower layer of charcoal, and more charcoal is added as required. The impurities are oxidized by the usual cold blast. The product is said to have high purity.—W. A. H.

GILLED TUBING

"Sauerbier" patent spiral-gilled tubing for heating, drying and refrigerating plants is being manufactured in Germany from seamless Siemens-Martin steel tubes with corrugated spiral gills, the whole being galvanized. It is claimed that this tubing has a large heating surface combined with great strength.

THE TOXICITY OF WHITE LEAD

Line (*Drugs, Oils and Paints*, 28, 255) reports that a large decrease in plumbism in the manufacture of white lead has followed the abolition of female labor and youthful labor in England. The decrease is also consequent on ventilation, the

use of respirators, overalls, enforced cleanliness, and the avoidance of lead dust. No material increase in the cost of manufacture has resulted, but death and suffering have been averted. Plumbism is usually easy to diagnose, yet lead occasionally induces obscure affections of the nervous system, the cause and true nature of which are not always recognized. The grinding of white lead with oil was formerly a large source of lead poisoning, because the pigment was dry, and consequently the grinding mill attendants and the lead work laborers inhaled lead carbonate dust; but since in many factories the paint is now made with the lead carbonate in the moist state, by gradually displacing the moisture with oil during the process of grinding, this source of danger has decreased. There is said to be more danger in the process of grinding basic lead sulfate into paint oil than there is when grinding the moist lead carbonate in oil. Line emphasizes the dangers incidental to the manufacture of red lead, these being referred to as "terrible."

TANTALUM AS A SUBSTITUTE FOR PLATINUM

In a paper on "Tantalum Electrodes," published in the *Chemiker-Zeitung*, 36, No. 126, 1233, O. Brunck discusses the substitutes for platinum and the employment of tantalum as a partial substitute for this costly yet valuable metal.

As there is little prospect that the price of platinum will ever decline to any considerable extent, science and industry have made strenuous efforts to obtain a substitute. Quartz glass at a moderate price offers, for certain purposes, a substitute for platinum, although not quite its equivalent. It is resistant to acids, with the exception of hydrofluoric acid, and is insensible to sudden changes of temperature, but it is breakable and is a poor conductor of heat. Chemical apparatus has also been made of an alloy of 90 per cent. gold and 10 per cent. platinum; this alloy is harder and tougher than gold, but is, unfortunately, more difficult to work than either one of the component metals. It is likely that it might replace platinum entirely if its melting-point were higher; as it is, its scope of application is large enough, but the economy attained is small, for the price of apparatus constructed of it amounts to about two-thirds of that of platinum, owing to the higher cost of molding.

A German concern has recently proposed tantalum, originally intended only for the manufacture of metal filaments for electric incandescent lamps, as a partial substitute for platinum, and has put on the market various forms of apparatus and instruments made out of that metal at a price of \$0.625 per gram, including cost of molding. As a material for surgical and dental instruments tantalum has already found favor with practitioners; but in chemical laboratories, tantalum dishes are, so far, the only form in which the metal is employed. Brunck states that the sensibility of tantalum to oxygen at the higher temperatures and to hydrofluoric acid prohibits a more general use of the metal as a platinum substitute. In a vacuum tantalum will stand the highest white heat, but, heated in the air, it commences to oxidize below a red heat; and while it is perfectly resistant to water solutions of alkalis, the compact metal is destroyed by fused alkalis.

Experiments conducted by Brunck showed that tantalum could be substituted for platinum as cathode material without reserve, while this was not the case with regard to anodes. He found, however, that if it was desired to use tantalum as anode material and to work with a tantalum cathode and a platinum anode, the tantalum anode might be plated with a thin layer of platinum which could be easily accomplished electrolytically. A coating of a few centigrams of platinum was found to suffice. It was found to be even better to employ an anode of tantalum wire which was plated with platinum by a process patented by Siemens and Halske. Brunck reports that tantalum has even some advantages over platinum as cathode material; for example, zinc and cadmium show no dis-

position to enter into an alloy with tantalum on its surface, hence there is no need of the cathode being plated with copper or silver as in the case of a platinum cathode. The insensibility of tantalum to *aqua regia* permits the removal of platinum and gold precipitate by that acid. A further advantage of tantalum over platinum is its greater strength and rigidity which prevents the electrodes from getting out of shape by bending. The difference in price is noteworthy, that of tantalum being 40 per cent. less than that of platinum. There is also a saving in weight of about 30 per cent. Brunck considers that tantalum may serve as a substitute for platinum in the different types of bleaching electrolyses.

SULFUR IN ILLUMINATING GAS

L. J. Willien (*Gas Age*, 31, No. 1, 5) points out that in a plant, where both coal gas and carburetted water gas are manufactured, a high percentage of sulfur in the coal has a twofold, and possibly threefold, evil effect, namely: (1) In almost every case a high sulfur content of the gas will be found, both in hydrogen sulfide and carbon disulfide; (2) When the coke is used in the generator of a water gas machine, about 50 per cent. of the sulfur in the coke goes into the gas, so that the sulfur which is not given off in the coal gas will be given off in the water gas; (3) A coal containing a high percentage of sulfur usually contains a high percentage of iron, which will cause clinkering trouble when the coke is used in making water gas. By knowing the percentage of sulfur in a coal or coke, the amount of sulfur compounds that the unpurified gas will contain can be approximately estimated in the following manner: With coal gas, multiply the percentage of sulfur by 20 and the product will be grains per 100 cubic feet of sulfur compounds in the unpurified gas. With water gas, multiply the percentage of sulfur in the coke by 10 and the product will represent grains of sulfur compounds per 100 cubic feet.

In using lime for removing carbon disulfide, while it is necessary to remove the carbon dioxide from the gas, still it is not economical to remove carbon dioxide by passing through a lime box. With six purifying boxes connected so that they can be used in any combination, the most economical method of operation is to fill four of them with oxide and two with fresh lime; allow the crude gas to pass through one of the fresh lime boxes for 24 hours to partially sulfide the lime; have the gas pass through two oxide boxes first, in order to remove hydrogen sulfide, then through the fresh lime to eliminate carbon dioxide, then through the lime box containing partially sulfided lime to remove carbon disulfide, and finally pass through one of the other two boxes filled with oxide, keeping one oxide box in readiness to be cut in when necessary. Where the amount of sulfur compounds allowed in the gas is limited to 30 grains per 100 cubic feet, it is hardly safe to use a coal containing more than 2 per cent. of sulfur and keep within the limit by using lime. Where the limit is 20 grains, the coal used should not contain more than 1.5 per cent. of sulfur.

THE USE OF GASES FOR FIRE EXTINCTION ON BOARD SHIP

A discussion on the use of gases for fire-extinction and fumigation on board ship took place at the meeting of the British Institute of Marine Engineers on November 25, 1912. A report of such parts of this as are of interest to the chemical engineer is presented below.

G. Canning said he thought that the practice of blowing steam into the cargo could be regarded only as a check to initial outbreaks. It had been said that the danger to human beings of systems in which odorless gases were used, could be overcome by impregnating the gas, but such a procedure depended a great deal upon the operator. Canning considered that the possibility of a deposit taking place in the pipes was more likely

in the case of flue gas than in the sulfur dioxide apparatus. In his opinion, sulfur dioxide was also more efficacious for fumigation purposes.

P. Selow said that with the carbon dioxide system ten cylinders, each of 40 pounds of liquefied gas, would be sufficient to deal with a space of about 42,000 cubic feet. The average number of cylinders supplied to a vessel was 50, and the cost of a new installation should not be more than \$1750.00 at the outside.

Prof. Armstrong said that carbon dioxide, sulfur dioxide, steam, and flue gas systems were all based upon the same principle—the reduction of oxygen in the air. The carbon dioxide system required a somewhat expensive equipment of iron cylinders filled with the compressed gas, and there was the disadvantage that when the supply was exhausted, as it might be on a long voyage, the system would be valueless. The same difficulty occurred in the case of the sulfur dioxide system, with the additional objection that the use of sulfur dioxide would injuriously affect the metal-work of the ship and certain cargoes. Steam had the advantage that it was always there as long as the boilers were at work. The flue gas system also had that advantage and was very ingenious, as it utilized a waste material, which could be obtained as long as the coal supply lasted, and which had practically the same power as the other gases of acting as an extinctive agent, while it was without their deleterious effect on the cargo.

J. Craig stated that the temperature of the flue gas was reduced to about 100° F. when put into the cargo. There was, he maintained, no deposit in the pipes with this system. He pointed out that a cooling process was necessary in fire extinction.

K. Scott considered the use of inert gases as of particular value for the prevention of spontaneous combustion in cargoes of coal, cotton and wool. He called attention to the fact that a distinctive odor could be imparted to inert gases by the addition of carbon disulfide, mustard oil, etc., and that the fumigating power might be thus increased.

A NEW TIMBER PRESERVING PROCESS

In the process for the preservation of timber devised by R. A. Marr, the preservative material is melted paraffin with silica in suspension, together with a small amount of naphthalene. The silica used is diatomaceous earth of which 92 per cent. will pass 200 meshes to the linear inch. It is said (*Eng. Min. J.*, 94, 1125) that wood can be permeated to the center, regardless of the dimensions of the timber, in a maximum of four hours as against 12 to 24 hours for creosoting. It is claimed that the treatment will prevent checking, adds resilience to the timber, and renders it immune to the attacks of the teredo and other marine borers, owing to the hardness of the silica. It is also claimed that the treatment is successful with white oak and other hard woods which are impenetrable by other processes. The process is an open-tank one, the experimental plant consisting of a vertical cylindrical tank just large enough to admit a railroad tie and jacketed to retain the heat supplied by a gasoline burner beneath the tank. The tank holds about 125 pounds of the preservative mixture, which costs about \$0.03 per pound. For complete impregnation of oak and pine it requires about 1.65 to 2.00 pounds of solution per cubic foot of timber. Spikes and nails are said to hold better than in creosoted or in untreated wood, and not to rust; and the treated wood does not become waterlogged under any conditions of use.

THE BILLITER ALKALI-CHLORINE CELLS

Allmand (*Chem. News*, 106, 291) reports that J. Billiter, of the University of Vienna, has designed two successful types of non-mercury alkali-chlorine cells. The Billiter-Siemens cell has already been described in several places. It has diaphragms, these being placed horizontally instead of vertically, as is gener-

ally the case. The floor space required is greater, but the diaphragms are stabler chemically and the current efficiencies are high. Several installations of this cell are working on the Continent and in America. The Billiter-Leykam cell is a modified bell-jar cell. The cathodes are, however, arranged underneath the bell-jar, being contained in porous asbestos hoods to catch the hydrogen. The brine leaving the cell does not therefore change the direction of its motion before reaching the cathodes. A far more uniform flow is thus obtained, and the current efficiency is high in result thereof. It is said that the porous asbestos hoods offer very little resistance to the passage of the current. The cell, being furthermore heated by means of hot liquids flowing through earthenware pipes, requires low voltage. At 85°, 12 to 13 per cent. of sodium hydroxide can be made at 92 per cent. current efficiency, employing 3.1 volts. Attendance charges are low and unpurified brine is used. The first installation at Gratwein, Austria, is said to work very satisfactorily.

WATER PURIFICATION IN THE INDUSTRIES

In *The Chemical Trade Journal*, Royal-Dawson states that the best way to keep a boiler as free as possible from sediment is by forcing air through it and greasing the inside with petroleum. A good way is to add petroleum to the water, and this directly avoids the formation of scale. Heavier oils are not to be recommended, as they tend to form fatty acids on dissociation at the high temperature and pressure at which boilers are worked. Fatty acids form a thick coat on the sides of the plant, and in time corrode the metal.

The general method is to use a mixture of soda and lime. The soda precipitates the lime salts as insoluble carbonate of lime, and the lime in a slaked form, or lime water, decomposes the bicarbonates. If the water be heated it can be purified by soda alone, when calcium sulfate is precipitated and the bicarbonates are decomposed by the heat. It is the custom to purify feed waters before they enter the boiler, and only such water as is clear and free from sediment should be used. If such treatment of boiler feed waters were systematically done, and put under proper continual chemical control, the cost of fuel for heating would be greatly lessened, and the life of a boiler would be no anxiety to the chemical engineer.

It is a good recommendation that the works chemist should include in his daily routine of ordinary tests outside the laboratory that of testing the water in boilers for acidity or alkalinity, and have a certain standard to go by.

With regard to trade effluents, the same author goes on to say:

The drainage from breweries varies considerably, but it chiefly comes from the 'coppers,' or boiling vats, consisting of hop refuse and soluble nitrogen compounds. The water hardly requires chemical treatment, being so dilute, but in case of necessity a mixture of lime and alumina is recommended.

"Pyrites pits waste contains ferrous sulfate and sulfuric acid in the drainage water. By treatment with oxide of lime, crude gypsum could be obtained in the usual way.

"The refuse water from tanneries contains decomposed animal matter. Sulfide of lime, and arsenic from the use of sheep dips, may also be found. In this case clarification with lime and sulfate of iron, and filtration afterwards, is to be recommended.

"The refuse of the Leblanc soda process, when dried, could either be used as a manure or worked up into other products. The waste effluents from the ammonia soda process contains much calcium and sodium chloride, and from these constituents hydrochloric acid and free chlorine can be produced."

THE SLATE-BED TREATMENT OF SEWAGE

At the Ordinary Meeting of the London Section of the Society of Chemical Industry, on December 2, 1912, W. J. Dibdin gave an account of the success of the slate-bed process. The introduction of this process marks the utilization of one waste product,

slate *débris*, to effect the conversion of offensive organic waste into an inoffensive earthy form having some manurial value. The action of the slate-beds are summarized as follows: The solid matters in the sewage are allowed to settle on shelves of slate supported by slate blocks at a distance of about two inches, these being superposed to a depth of one to five or six feet as required. In consequence of the alternate filling and emptying and resting empty, the deposit becomes the home of many types of organisms that digest the matters and render them inoffensive in like manner to the action by which earthworms produce a humus from organic *débris*, and throw it to the surface in the form of worm-casts. In the slate-bed the deposit of earthy matter thus formed on the surface of the layer of mud on the slates is washed off by the receding effluent when the bed is emptied, and forms a black slurry, consisting of mineral and indigestible matter with numerous organisms from the bed. This slurry is then placed on a suitable drainage bed for the water to drain off and to allow time for the full digestion of any crude material that may have come from the bed, and, finally, to allow the host of infusoria gradually to extinguish themselves by the natural process of the "survival of the fittest." As a result of experiments during a period of eighteen months at High Wycombe, England, it was found that the quantity of residual matter was equal to only 3.4 tons of 90 per cent. moisture per million gallons of normal sewage. "On the assumption that farmers will remove the air-dried humus at their own cost, the capitalized annual economy will repay the cost of the slate-beds." The nuisance of sludge disposal is also abolished.

THE MANUFACTURE OF SWEDISH FILTER PAPER

Fornstedt (*Paper*, 10, No. 3, 17) describes the processes involved in the manufacture of filter paper in Sweden.

Machine-made filter paper is used chiefly in the household and for technical purposes, while hand-made filter paper for scientific analyses is of better quality, though of different grades and make, according to the character of the analysis to be made. The paper being more or less quick-filtering it is made with regard to whether a mere purification of the liquid is intended or whether the substances collected on the paper are to be qualitatively or quantitatively determined.

Some qualities of filter paper, as white and gray woolen paper, are made generally in small paper mills which are not equipped with steam boilers. The rag is furnished "raw" in the beaters and beaten free, but care is taken to avoid lumps. The paper is made on a cylinder machine and taken wet on the hasp from where it is cut by hand and hung up for drying. A rough mottled surface is produced by means of a coarse wire cylinder running on the wet paper web, the impression remaining very plainly after the paper is air-dried.

The cleanest rag is used for filter paper, and it must be of the best quality and sorted carefully. Iron is, of course, one of the worst impurities in a filtering paper. The rag is boiled with sodium hydroxide, as it gives a lower percentage of ash than lime; and for bleaching a mixture of manganese dioxide (8 parts), sodium chloride (6 parts), and sulfuric acid (5 parts) is used in lead retorts. After the rag is boiled, washed and beaten to halfstuff, it is dried in a centrifugal drier and spread in layers on wooden poles in the bleaching chamber. This chamber is of concrete, lined with wood. After the bleaching chamber is filled with halfstuff, the door is closed and chlorine is admitted through an aperture in the roof. After all air has been expelled, the chamber is well sealed, and the halfstuff, after absorbing the chlorine for several hours, is effectively bleached. Liquefied chlorine is now used in some mills in this bleaching process.

The analysis of boiled and bleached halfstuff shows the following ash percentages (silica and lime):

New shirt cuttings, No. 1.....	0.039
Old linen, white.....	0.132
Old linen, gray.....	0.140
Colored cottons.....	0.177
White cottons.....	0.107
Sulfite, bleached.....	0.298
Soda, bleached.....	0.4

It is, of course, a matter of great importance that the water used in the manufacture of filter paper should be as pure as possible, but it is impossible to avoid some ash-containing matter from being introduced to the halfstuff with the water of manufacture and in the transportation of the halfstuff and the process of drying. Generally the increase is from 0.02 to 0.05 per cent., depending on the state of the weather and the condition of the water.

The time consumed in beating varies according to the nature of the material. Halfstuff freshly bleached requires a longer time than that which has been stored some time. Neither too free nor too slow stuff should be used for filter paper. Stuff that is too slow retards filtration—meaning the time taken for a given quantity of water of a certain temperature to filter through a paper of specific diameter. Paper made of too free stuff fails to keep back the finer grained sediments, such as sulfate of barium, etc.

Among the considerations to keep in mind in the manufacture of filter paper are the rate of filtration demanded, the ash content, resistance to sulfate of barium, fine holes, weight, and impurities.

To produce a filter paper of low-ash percentage requires treatment with hydrochloric or hydrofluoric acid or a mixture of these acids, which will remove impurities like ferric oxide, alumina, lime, magnesia and silica, and paper so treated is practically a pure cellulose paper. With hydrofluoric acid silica is removed, and with hydrochloric acid the other substances enumerated are dissolved away. After treatment with acids the paper should be thoroughly washed with distilled water to remove the last traces of acidity.

To test the neutral reaction of the paper after washing, a solution of nitrate of silver is used to advantage. The wet paper is squeezed with the hand over a glass funnel and the water filtered into a test tube. In another test tube containing distilled water a few drops of test solution of nitrate of silver are added, and the same quantity is added to the water expressed from the washed filter paper. The two tubes are then compared against a black background. If not neutral the water from the filter paper will show an opalescence due to the chlorides remaining in the paper, and further washing is necessary. After this treatment the paper is pressed and hung out in open barns in order to freeze it.

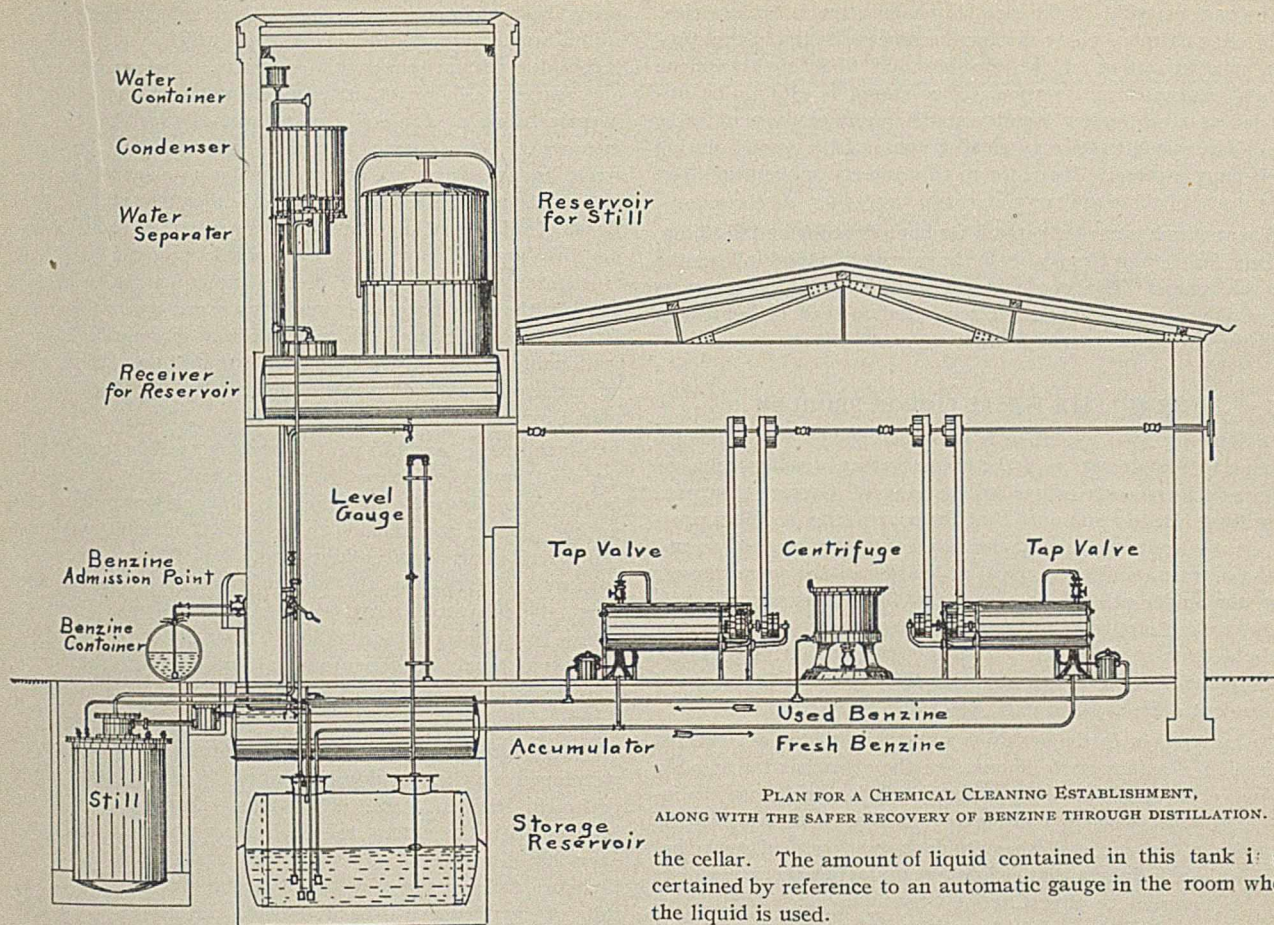
By freezing, the paper is made soft and porous, since the ice crystals formed in it serve to drive the fibers apart. Because of this the finest qualities of filter paper only can be made in the winter time in cold countries.

Experiments have been tried of subjecting paper that has been dried in a warm atmosphere to a subsequent freezing operation in order to impart the desired softness and porosity, but it has been found that paper treated in this way does not become soft and it never comes up to the standard of the best Swedish filter paper.

THE MINIMIZATION OF FIRE RISKS IN THE CASE OF INFLAMMABLE LIQUIDS

A Berlin firm is manufacturing plants for minimizing and preventing risks from fire or explosions in industries where inflammable or explosive liquids are employed.

The inflammable liquid, for instance, benzene, flows out of the tap, as desired, under the normal pressure of protecting gases. The pipes and valves are protected against injury, and the taps



PLAN FOR A CHEMICAL CLEANING ESTABLISHMENT, ALONG WITH THE SAFER RECOVERY OF BENZINE THROUGH DISTILLATION.

can, in the case of garages, etc., be put in any part of a building as desired. In cases wherein large quantities of the inflammable liquid are to be stored, the storage-tank is located underneath

the cellar. The amount of liquid contained in this tank is ascertained by reference to an automatic gauge in the room where the liquid is used.

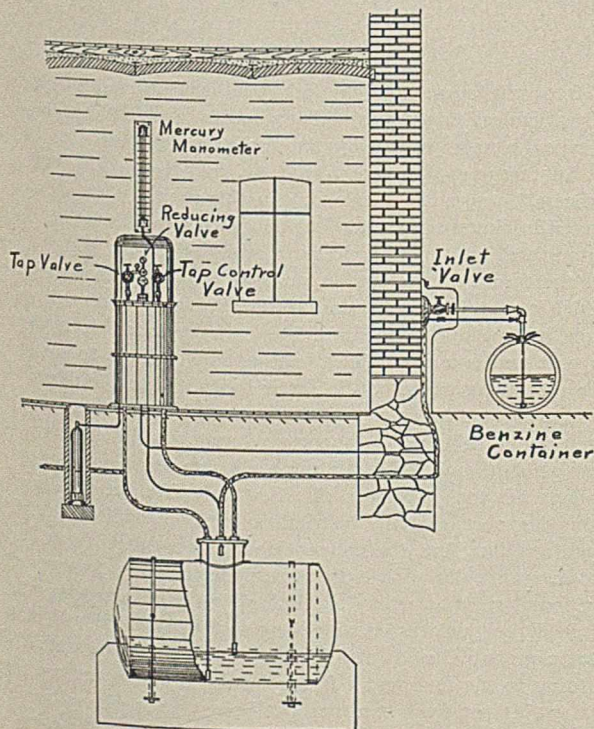
THE BRITISH STARCH INDUSTRY

The cornstarch industry of America has been dealt with in several papers published in the *Journal of the Society of Chemical Industry* (see *Ibid.*, 1900, 617; 1902, 4; 1909, 343; and 1910, 527), but the starch industry of Great Britain has just recently been discussed by Traquair (*Idem.*, 31, No. 21, 1016).

The maize starch industry is centered in Paisley, Scotland, rice starch manufacture is located in England, while Ireland produces the whole of the wheat starch. At one time there were some 10 plants manufacturing maize starch in Paisley and neighborhood; at present there are 5. These grind about 600 tons of Indian corn weekly and produce about 20,000 tons of starch and corn flour annually. The process of manufacture is practically identical with that employed in America.

Traquair states that the future development of the maize starch industry seems to lie along the line of (1) technical utilization of the maize glutes; (2) the application of diastatic conversion to the production of starch sugar in a concentrated solution; and (3) new acid conversion methods and products. The peculiarity of the British position is that the corn is all imported and shows a wide diversity of quality and origin. This state of affairs calls for some flexibility in the process to enable the best results to be obtained.

The present position of the industry is said to be a precarious one. The import of American maize starch exceeds the home production, and represents the surplus of the enormous production of the United States; it is frequently sold at a price which hardly covers the cost of production. This policy has resulted in the closing of the smaller starch works and has forced the others to go in for special products and treat American pearl starch more as a raw material than a manufactured article. The total export of maize starch from America in 1911 was 37,430 tons, of which 92 per cent. went to Great Britain.



CROSS-SECTION OF AN AUTOMOBILE GARAGE PROVIDED WITH SAFETY DEVICES FOR MINIMIZING RISK FROM FIRE
The same scheme may be applied to industries wherein benzine is used

The raw material of the rice starch industry is broken rice, and from a chemical point of view the process is simply the solution and separation of the proteids and fiber by treatment with a weak alkaline solution. Rice starch is said to be unequaled as a cold water laundry starch, as it easily penetrates the fabric, owing to its very small granule and is swollen during the ironing process. There are 10 to 12 plants in operation, but only 3 or 4 of these are large.

Wheat starch is the best starch for linen dressing and finishing, and the location of two plants in the north of Ireland follows the natural course. The raw material in the modern process is wheat flour, and the gluten is recovered instead of being lost as in the old fermentation process.

THE SULFITE WASTE LIQUOR PROBLEM

In THIS JOURNAL (5, 78-9) is published some correspondence relating to the utilization of the waste liquors of sulfite cellulose mills which recently appeared in several German journals. It is of interest to again note that the controversy is still in progress in the columns of our foreign contemporaries in regard to the practical and economical utilization of the waste liquors from the sulfite cellulose process, and the author of an article in *Papier Zeitung*, which a later correspondent criticized, comes to the defense of his paper in a recent issue of that publication, in a communication that forms an addition to the literature of the subject. He says, in part, according to *Papier*:

"In no respect is the article in question directed against the utilization of sulfite waste liquors; on the other hand a possibly profitable process is heartily recommended to cellulose manufacturers. But when a daily paper of the importance of the *Frankfurter Zeitung* publishes inadequately verified technical articles, there is danger that cellulose manufacturers or capitalists may be tempted to invest money fruitlessly in waste liquor utilizations. And there should particularly be a warning against the production of products of low value that afford no promise of interest on capital.

"Such, however, is notably the process of coal briquetting with unpurified waste liquor, rich in ash, which is commended in the *Frankfurter Zeitung*. There is no significance in the fact that Privy Mining Councilor Francke has written on the subject in 1910; rather this is proof of the slight extent to which the value of the experiences described has been recognized. Even the *Frankfurter Zeitung* is as yet unfamiliar with the failures that have been encountered in the employment of unpurified sulfite waste liquors and cellulose pitch in coal briquetting. Neither neutral concentrated cellulose pitch nor acid concentrated waste liquor furnish unobjectionable briquettes; only purified, consequently to a certain extent ashless, liquor could be employed for coal briquetting. Almost all the large German banks have had propositions for coal briquetting with sulfite waste liquors submitted to them and the unanimous opinion of experts has been to the effect that the briquettes were of low value or unfit for use."

How waste liquors could be freed from acid or purified, it was not the purport of this paper to discuss, the author continues; it was intended only to warn against extravagant expectations, for, until to-day, the commercial value of sulfite briquettes has been nowhere proven. In cellulose manufacturing circles so far, the more rational decision has been arrived at to profit by the failures of others before throwing away money on undertakings devoid of prospect.

Against ore-briquetting with sulfite waste liquors nothing is said, only the fact is noted that the few furnaces that have so far used the process, have kept their experience secret and that, for this purpose, license-free concentrated sulfite waste liquors can be used just as well as patented, solid cellulose pitch.

"If the agriculturist wishes to obtain lime for fertilizing pur-

poses, he can do so cheaper by methods other than the use of sulfite waste liquors, the product of which, under the most favorable circumstances, is gypsum. Agricultural expert authorities are, however, uttering earnest warnings against the overplastering of the soil (by means of superphosphate, for instance). The organic nutritive substances of the sulfite waste liquors, which are always of value to plant life, have not hitherto been furnished to the farmer in their best available form. Least of all are cellulose pitch or concentrated liquor adapted for this purpose, for their hygroscopic properties and their crust-forming tendency are serious disadvantages, apart from the fact that the material is much too expensive for the farmer. If sulfite waste liquors are to be utilized in agriculture, unobjectionable products must first be obtained from them. The advertisement of sulfite-waste liquor that has been concentrated by any means is no assistance.

"Against the possibility of 'donating' sulfite waste liquors for road sprinkling, there is no objection to be made. But in the *Frankfurter Zeitung* there is no mention made of 'donating,' rather the millions to be earned in Germany by concentrating plants was enlarged on. For this reason, to prevent misunderstanding, the fact was mentioned, that the cities, in spite of exhaustive tests, would have nothing to do with waste-sulfite liquor for road sprinkling. They prefer to use chloride of calcium, because experience with it has been more satisfactory. The disinfectant properties of sulfite liquor are also exposed to grave doubt.

"The utilization of sulfite liquors for tanning extracts was not mentioned by the *Frankfurter Zeitung*, therefore there was no reason to refer to them. The writer referred to said he was familiar with the extent to which among tanners and leather chemists, controversy rages for and against their use. It is therefore the work of these trade authorities to collect the results of experience in this new field. If the new tanning extract proves satisfactory, the German technique can be trusted to make use of it because for the tanning substances now most in use duty must be paid. On sulfite liquor-tanning extract from abroad duty would also have to be paid."

"SACCHULOSE"

It is well known that the industrial utilization of the alternative chemical substances which wood is capable of yielding has received a new impetus by the application of several processes. A. Zimmermann (*Chem. Trade J.*, 51, 588) discusses the "Classen process," as used in England. In this process sawdust is subjected in closed retorts to digestion with a weak solution of sulfurous acid and under a pressure of about 6 to 7 atmospheres. Of the resulting product, sugar is an important constituent, of which it contains about 25 per cent. This sugar is drawn equally from the soluble and insoluble carbohydrates; it is dextro in part and is fermentable to the extent of about 80 per cent, the rest being pentose. So far it has not been possible to obtain a crystalline sugar on a commercial scale. According to the original scheme, the sugar produced was, in effect, worked into alcohol, and the maximum yield was about 30 to 35 proof gallons per ton of wood. The English Spirit Act of 1880 contains, however, so many restrictions in the manufacture of spirit from anything but the conventional sources that it was found to be practically useless to pursue the matter. Zimmermann has found wood sugar, or "sacchulose," to be of value as an article of food, particularly as a feeding-stuff for horses, and states that a probable use is also in the preparation of caramel. According to his findings, a factory capable of treating 200 tons of sawdust per week can turn out between 300,000 and 400,000 gallons of proof spirit per year. This also gives by-products of 50 tons of acetic acid, 10 tons of furfural, and 2,000 gallons of methyl alcohol for recovery.

NOTES AND CORRESPONDENCE

A STANDARD VISCOSIMETER AND STANDARD METHODS FOR DETERMINING VISCOSITIES—WHY NOT?

Editor of the Journal of Industrial and Engineering Chemistry:

Although the unsatisfactory condition which exists in this country, in the determination of the viscosities of lubricating oils, was emphasized in the report of Committee D-2 on Standard Tests for Lubricants (*Proc. Am. Soc. Testing Materials*, 10, 117-146), no action has since been taken to improve the situation. The writer does not know just what official action could best be taken, but he believes that he expresses the opinion of most chemists interested in the oil-distributing industry, when he states that the condition is eminently unsatisfactory.

Aside from the use of a large number of types of viscosimeters, which must of necessity occasion unnecessary work in checking up oils for specifications, there is the more serious defect, that no adequate provision seems to be made for standardizing viscosimeters of a given kind. The data included in the report (*Ibid.*) show that variations of 20-30 per cent. in the viscosities reported by the different analysts, for the same oils under the same conditions, are not infrequent. It would seem that differences as large as these must be due, in the main, to a lack of agreement between the viscosimeters. In the relatively small number of comparative tests which the writer has had with other analysts, checks within 3 per cent. as a maximum variation have been obtained. Each analyst with his own viscosimeter would, of course, get values agreeing to 1 or 2 per cent.

The situation in Germany, in particular, would seem to be much better. The almost universal use of Engler's viscosimeter, together with the provisions made for its accurate construction and standardization and with the reference tables such as those of Ubbelohde, must insure better working conditions for the trade. From these tables it appears that the extreme variations for different instruments are 4 per cent. (50-52 seconds water value at 20°). Moreover, by employing the certified water value, which may be checked from time to time, it is possible to obtain from the tables, the Engler numbers, or the corresponding absolute values, which are certainly accurate to a much smaller percentage. The saving of time made possible by running only 50 or 100 cc. of oil, and also the possibility of checking the regularity of the course of a determination, are desirable features, which the use of the tables affords.

Since the Saybolt instruments are not obtainable in the open market, and the Tagliabue instrument seems to be unreliable and faulty in design (Report of Committee D-2, *Ibid.*), it would seem desirable that the Engler viscosimeter be adopted in this country. One or two objections may be advanced against the Engler, but these are unquestionably more than offset by its many advantages. The recommendation of Ostwald's viscosimeter by Dunstan (*J. Soc. Chem. Ind.*, 31, 1063-4) would probably not be received favorably by the trade here, although his suggestion that determinations be made at several widely differing temperatures, is a good one (now complied with to a certain extent). The results obtained by Ellis (*Met. Chem. Eng.*, 10, 546) should be especially valuable if a satisfactory apparatus, such as Engler's, were adopted, provided that the Temperature-Viscosity Law proves to hold for oils of widely different character. In this connection, it might be stated that a more definite conception of the "temperature of complete solidification," and a full description of the proper method for determining this value, are desirable.

Curves similar to those obtained by Gray (*Original Communication, Eighth International Congress of Applied Chemistry*, 10, 153-8) are useful, and have been employed in our laboratory for some time, but their usefulness is impaired by the lack

of uniformity between different viscosimeters of the same type.

Until some reliable standard instrument is adopted, it would seem useless to attempt the preparation of tables and curves, analogous to those of Ubbelohde. This conclusion is based upon the unsatisfactory data obtained by Committee D-2, and on the failure of data obtained in our laboratory to check even approximately with some of the curves given in the report (*Ibid.*).

Fig. 12, in the report, is improperly labeled, and some of the curves do not check with the data, owing to the fact that the proof was not submitted to the chairman, Dr. Gill, and the publishers saw fit to change the cuts submitted to them. (Private communication from Dr. Gill.) Fig. 13, showing the relations between the different viscosimeters at 212° F., indicates that the Saybolt Universal values should be somewhat more than twice those obtained with the Saybolt C instrument. The following values, taken from our note-books, are not in accord with this requirement. In these tests, no precautions other than those usually observed for maintaining constant temperatures, measuring the oil, and taking the time with a stop-watch, were taken.

TEMPERATURE 210° F.

OIL	SAYBOLT C	SAYBOLT UNIVERSAL
D. W.	40"	42"
P. A.	42 ¹ / ₅ "	46"
P. R.	54 ¹ / ₅ "	55 ³ / ₅ "
E. F. G. ¹	134"	127"
C. S. ¹	148"	132"
M. S. R. ¹	233 ¹ / ₅ "	227 ² / ₅ "

¹ These values were not obtained from the same sample of oil, but from different lots of the same oils, which have always shown only small variations from lot to lot.

Dr. Gill kindly had a sample of P. R. (from the same lot) run in his laboratory, and reported a viscosity of 54³/₅" at 210°, Saybolt C. He checked our Universal viscosimeter at 100° F., and we have also had several satisfactory checks with technical analysts on both the Saybolt C and Universal instruments. It is improbable, however, that satisfactory checks would be obtained with any large number of analysts, in view of the lack of concordance indicated in the above mentioned report.

The writer has written this note for the purpose of once more calling attention to the unsatisfactory condition in the determination of viscosities, and trusts that others may interest themselves to the extent of working out some adequate solution of the difficulty.

W. F. FARAGHER

LABORATORY OF THE ALDEN SPEARE'S SONS CO.
BOSTON, Jan. 15, 1913

THE USE OF A LIGHT FILTER CELL IN POLARIZING HIGH GRADE SUGARS¹

Explicit directions for the polarization of sugars as to normal weight, graduation of sugar flask, clarifiers, temperature of polarization, and the sources of light, are given by the International Commission for Uniform Methods of Sugar Analysis but no mention is made of a light filter cell to be used with the prescribed sources of white light. It may be deemed by some a necessity too well known to be mentioned, yet many sugar chemists do not know that without its use an error is introduced. The purpose of the light filter cell is to correct the difference in rotation dispersion between sucrose and quartz. The blue and violet end of the spectrum causes the greatest amount of rotation dispersion and these rays are easily absorbed when the light is passed through a solution of neutral bichromate of potash.

¹ Read at the 7th meeting of the International Commission for Uniform Methods of Sugar Analysis held in New York City, September 10, 1912.

Dark colored sugar solutions naturally tend to purify the light but with light colored solutions there is little purification. When these blue and violet rays are not cut off the polarization is always higher than when they are removed. In some cases an increase of as much as 0.3° V. has been noted. Schönrock¹ noted an average increase with some observers of 0.127° V. He recommends as a filter a 6 per cent. solution of bichromate in a cell $1\frac{1}{2}$ cm. long. Browne² found that the average difference between the readings of the lowest of 4 observers, when using a 3 per cent. solution in a 3 cm. column, was 0.03° V. while with no cell it was 0.22° V. and with a 1 per cent. solution in a 3 cm. cell it was 0.08° V. From this it is seen that results are made concordant by the use of a 3 per cent. solution in a 3 cm. column or by using a solution of such strength that the percentage multiplied by the length in centimeters is 9.

Most makers of polariscopes include in their apparatus either a light filter cell or a crystal of bichromate placed in the ocular but in their directions accompanying the instruments no particular mention is made of the use of the cell. Letters addressed to foreign sugar chemists regarding the use of a light filter cell brought the following replies.

Dr. A. Herzfeld, of the Institute for Sugar Industry, Berlin, Germany, writes:

"The bichromate filters in small tubes were introduced by me more than twenty years ago and that first in the Peters' instrument and later they were taken up by Schmidt and Haensch. They are not absolutely necessary in the investigation of colored sugar products by means of the half shadow instrument but they are absolutely necessary in the case of colorless sugar solutions. We use a $1\frac{1}{2}$ cm. layer of a 6 per cent. bichromate solution. * * * We remove the bichromate solution from the apparatus only in case very dark solutions are being examined in which it is just possible to adjust to a half shadow. I believe that the use of the ray filter cannot be avoided in electric or acetylene lights with colorless sugar solutions. A solution is always to be preferred over solid crystals, since it can easily be removed or renewed."

Dr. F. Strohmer, of the Chemical-Technical Experiment Station for the Austrian Beet Sugar Industry, Vienna, Austria, writes:

"We always use a bichromate cell in our polarization apparatus which is placed between the polarization apparatus and the source of light. * * * We have always had the best success with this arrangement and no differences at all have ever occurred. As a source of light we use a strong Auer or Nernst light and with such mixed lights I consider this arrangement necessary since by means of it the light, which is finally polarized, is homogenized."

Mr. H. C. Prinsen-Geerligns, of Amsterdam, Holland, writes: "The two hundred odd sugar laboratories in Java are organized and have the following rule:

"When moving the screw for the exact quality of color, the difficulty is often encountered that at the equal shading of the two halves of the discs, the color of both is not exactly the same, one-half possessing a red and the other a blue tinge. This very troublesome phenomenon, which hinders the exact ascertaining of the proper equality, is especially met with in the case of colorless or feebly colored solutions having to be polarized and is due to small differences in the optical properties of sucrose and quartz. In the old apparatus this trouble was neutralized by inserting a plate of transparent potassium bichromate in the ocular which absorbs the blue and violet rays and imparts a yellow color to the disc. In modern apparatus the plate is replaced by a solution of bichromate which is poured in a short observation tube of a very wide diameter which is inserted in the polariscope between the lamp and the lens and which may

be taken out to be made afresh. Working with sources of white light, *i. e.*, unfiltered electrical, Argand, Auer, kerosene and acetylene light, every separate observer finds values which are identical for his eye but which after experiments made by Schönrock may differ by 0.008 to 0.127° V. with those obtained by other operators when the polarizations are about 100, which clearly shows that by no means polarizations should be made with unfiltered white light. These differences disappear well nigh entirely if the light from the above mentioned sources is purified by allowing it to pass through a 6 per cent. solution of potassium bichromate in a layer of 6 cm. Hereby the difference in color between the two halves of the disc after the fixing of the just position, which is caused by the difference in dispersion between sucrose and quartz, is almost totally neutralized. In order to obtain by different operators fully concurring figures, it is indispensable to apply the aforementioned tube with potassium bichromate solution. Only in case the polariscope is not equipped with such a contrivance a plate of bichromate is to be inserted in the ocular. When polarizing dark colored solutions, the bichromate solution may be more diluted but it should never be left out."

"You see we are rather strict in Java."

Dr. H. Pellet, of Paris, France, writes:

"For the saccharimeter of the Schmidt and Haensch kind, it is necessary to use a light, slightly colored yellow by means of a cell of bichromate of potash more or less concentrated."

Dr. C. Fischma, member of the Board of Directors of the All-Russian Sugar Association, Kiebr, Russia, writes:

"We in Russia have no legal regulations concerning the use of bichromate of potash in sugar determination by polarizing. In the Association laboratory, however, a 5 per cent. solution of bichromate of potash is always used for the polarization of white sugar because it makes possible much more accurate polarization. In the polarization of yellow sugars, massacuites and molasses this laboratory does not use this solution."

Dr. Hugh Main, of London, England, writes:

"It is easier to read colorless solutions with a bichromate solution in the polariscope than without it and, therefore, I use it in testing the polariscope with pure sugar and retain it in position for all other polarizations."

In defining the 100 point of the Ventzke scale, the Imperial Reichsanstalt of Germany and the United States Bureau of Standards have adopted the use of this light filter cell. I recommend, therefore, to this Commission the following resolution:

That where white light is used in polarizations, the same shall be filtered through a neutral bichromate of potash solution of such a strength that the per cent. composition multiplied by the length of column in centimeters be 9.¹

A. HUGH BRYAN

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THE ANALYSIS OF UNSWEETENED EVAPORATED MILK.

Editor Journal of the Industrial and Engineering Chemistry:

We have had considerable difficulty in the fat determination of unsweetened evaporated milk by the Babcock method. To obtain good results directly on the milk, without modification in the manipulation, is an impossibility. Working on the diluted sample does not give satisfactory results. The Gottlieb method gives fair results, but it has been shown² that these results are uniformly low.

The method advocated by the Indiana Experiment Station in *Bulletin 134* gives good results, but they are not always uniform, much depending upon the milk with which one is dealing. The amount of acid, 17.6 cc., given in the method is too much in many cases.

¹ The Commission unanimously adopted this resolution September 10, 1912, at its Meeting in New York City.

² Indiana Expt. Sta., *Bull.* 134.

¹ *Ztg. Ver. d. Zuckerind.*, 54, 521-58 (1904).

² U. S. Dept. Agr., *Bur. Chem.*, *Bull.* 122, p. 222.

The following method, we have found, gives uniformly good results on all kinds of unsweetened evaporated milk.

I. MIXING THE SAMPLE

The sample is mixed by shaking, pouring and stirring; some globules of fat persist in staying unmixed; by looking across the surface of the milk with the eye in such a position that the light is reflected to it from the milk, one can easily detect these small chunks of fat and see whether the sample is homogeneous. If these chunks of fat will not mix, warming slightly (not over 40° C.) will help, or sometimes a sample will be met with that needs a very small pinch of caustic soda to aid in emulsifying the fat.

II. FAT

Weigh 4.5 grams of the well mixed sample into a 10 per cent. Babcock milk bottle. Add commercial sulfuric acid (sp. gr. about 1.8) of the same temperature, mixing the two with a whirling motion until a dark chocolate color is produced. From six to eight cubic centimeters of acid are usually necessary. Place the bottles in boiling water and heat for from fifteen to twenty minutes. Remove and let stand until nearly cold. Fill the bottle two-thirds full of hot dilute sulfuric acid (1 volume of water to 1 volume of the concentrated acid), and mix well. Place in the centrifuge and whirl five minutes. Fill to neck with hot half-strength sulfuric acid and whirl three minutes. Add hot water to bring the fat column into the neck of the bottle and whirl two minutes. Read at 120° F. to 125° F. from the bottom of the column to the extreme top of the meniscus. The reading multiplied by four gives the percentage of fat.

NOTES ON THE METHOD

1. In the condensing process the casein becomes toughened so that it is extremely difficult to get it dissolved in the sulfuric acid. The heating in the bottle with the sulfuric acid, and subsequent standing, aids in this process. There is little danger of charring if the correct amount of sulfuric acid is added.

2. If hot water is added before whirling, in most cases a precipitate forms which interferes with the determination. The addition of half-strength sulfuric acid prevents this.

3. Four and one-half grams were found to be the best amount with which to work.

4. The results obtained by this method have been very gratifying, giving uniformly good, clear readings that check well.

III. TOTAL SOLIDS

Weigh 1 gram of the well mixed milk into a tared aluminum milk dish. Add 25 cc. of water and evaporate to dryness on the steam or water bath. Dry to constant weight in a steam or water oven.

This method was found more satisfactory than making up a diluted sample of known strength and obtaining the sample for solids from it. It is simple and easy to manipulate.

KANSAS STATE AGRICULTURAL COLLEGE
MANHATTAN, Sept. 18, 1912

C. A. A. UTT¹

THE DETERMINATION OF "VOLATILE" IN COAL

Editor of the Journal of Industrial and Engineering Chemistry:

Much interesting and ingenious work has been done during the last two or three years on the determination of "volatile" in coal. It seems to me that his work is mistaken in that it attempts to patch up an inherently faulty method. The following determinations illustrate the weak point in the method.

These determinations were all made by the "official" method except that the flame was protected, and a Tyrell burner and a pipe clay triangle with projections were used.

In every case the flame was over 20 cm. in height and a good non-smoking flame. In No. 2 a Fletcher burner was burning on the same gas pipe as the determination but was put out before No. 3 was started; the regulators of gas and air on the burner were in the same position in each case.

Here are a number of analyses made with ordinary care, all complying, except as noted, with official directions and yet

there is a variation of 1.58 per cent. between the highest and the lowest. A rule should be so expressed that if it is followed good results *must* follow. It is not enough that good results *may* follow. It is, to say the least, conceivable that there would be greater difference of conditions in any two given laboratories than prevailed in my laboratory at the time when the Fletcher burner was burning and when it was not.

		Percentage volatile
No. 1	Very little gas.....	{ 20.90 21.20
No. 2	More gas than No. 1.....	{ 20.95 21.41
No. 3	Slight increase of gas over No. 2.....	{ 21.70 22.17
No. 4	More gas than No. 3.....	{ 21.40 21.65
No. 5	Same gas as No. 4—more air.....	{ 22.08 22.18
No. 6	Burner pushed to its utmost.....	{ 22.30 22.48

In my regular work I have always used a three-tube compound burner and have never had any difficulty in getting results agreeing within 0.2 per cent., the average difference between duplicates being 0.1 per cent. By my method the foregoing coal showed 22.67 per cent. and 22.57 per cent. I had attributed the close agreement of my results to the fact that all the coals which came under my observation were high-grade steam coals, New River or Pocahontas. I now believe that my method is, in part at least, responsible.

It is noticeable that as the results approach the limit, the agreement becomes better and it seems not unreasonable to infer that it is easier to get results when all the volatile matter is driven off than to stop at some point short of that result.

I am aware that the phrase "all the volatile matter" sounds loose and unscientific, but the following determinations show that there is a point not easily overstepped to which that definition may be applied.

The same coal was heated for increasing lengths of time according to my method, with the following results:

	Percentage volatile
8 minutes.....	{ 22.64 22.55
9 minutes.....	22.53
10 minutes.....	22.85

Applied to an anthracite coal, my method gave the following results:

	Percentage volatile
7 minutes.....	{ 5.00 4.98
8 minutes.....	5.02
9 minutes.....	5.00

Applied to a gas coal, the results were:

	Percentage volatile
7 minutes.....	{ 37.31 37.48
8 minutes.....	37.58

The slightly higher results which my method gives were not due to entrainment of solid particles. Both determinations gave:

	Percentage ash
Official method.....	4.40
In sample heated ten minutes.....	5.45

One thing that has been impressed on me during these experiments is the difficulty of judging, and consequently, defining, the heating power of a flame. I determined the first coal, a New River coal, and the anthracite with an ordinary Bunsen burner which I expected would give very low results. I obtained:

	Percentage volatile
New River coal.....	21.60 21.65
Anthracite.....	4.75 4.60 4.85

I tried determinations on these coals with the addition of

¹ Assistant Chemist Kansas State Board of Health.

kerosene, as suggested by Professor Parr,¹ and obtained 22.67 per cent. and 4.93 per cent., respectively. The addition of 7.6 per cent. water did not affect the accuracy of my results, but the addition of 22.8 per cent. water raised the percentage of volatile in the anthracite to 5.21 per cent. and 5.30 per cent., and in the New River coal to 23.00 per cent.

In view of the very limited number of coals at my disposal, I can only consider these figures as indications, but these indications certainly are that the rule for volatile determinations should be so altered as to compel the employment of sufficient heat. That an ordinary Bunsen burner does not give sufficient heat and that such an alteration in the rule would eliminate many sources of error.

I have spoken of heat. I do not know that my better results were not due to the fact that my crucible was well surrounded by reducing gases, but whatever the proximate cause, the ultimate cause was sufficiency of flame.

I am well aware that most chemists will hesitate to discard a process which has been in use so long, but any one who will take the trouble to read the modest disclaimer of the committee which suggested the method² will, I think, agree with me that it would be better to make a drastic revision of the rule in the sense, say, "heat at such a temperature that constant weight is reached in seven minutes," than to continue in the old unsatisfactory rut or bother with petty details.

I assume, of course, that the indications of this work are borne out in a more extended field.

I believe that I have shown that the rule for determination of volatile is not sufficiently explicit. The indications are that a more powerful burner than an ordinary Tyrell burner will give results a little higher, more concordant, and probably more significant. That the use of the larger burner makes the presence of ordinary amounts of water a matter of indifference.

That the use of the larger burner obviates the necessity for the use of kerosene. That a determination with the larger burner requires less care in regard to the time of the determination.

Since I wrote the foregoing, Messrs. Fieldner & Hall have published an article on the "Influence of Temperature on the Determination of Volatile Matter in Coal" in the Proceedings of the Eighth International Congress of Applied Chemistry. I have not yet had a chance to see this article.

FRED C. WELD

65 MERRIMAC ST., LOWELL, MASS.
October 15, 1912.

¹ THIS JOURNAL, 3, 900.

² J. Am. Chem. Soc., 21, 1116, et seq.

NEW CHIEF OF BUREAU OF CHEMISTRY

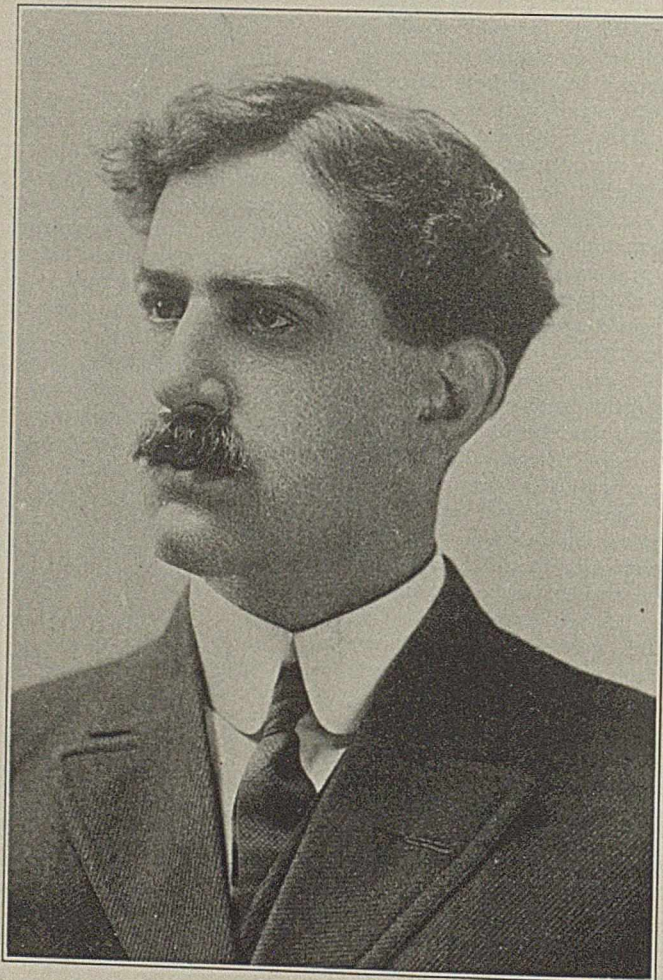
Carl L. Alsberg has been appointed Chief of the Bureau of Chemistry, United States Department of Agriculture, to succeed Dr. Harvey W. Wiley, resigned.

Dr. Alsberg was born in New York City, in 1877, and is the son of Meinhard Alsberg, a prominent chemist and one of the founders of the New York Chemical Society from which the American Chemical Society developed.

Carl L. Alsberg entered Columbia University in 1892 and received the degrees of A.B. (1896) and A.M. (1900); he also received the degree in medicine from the College of Physicians and Surgeons. During his residence in the medical school he became interested in biochemical research, and subsequently went abroad to study Pharmacology with Schmiedeberg,

Physiological Chemistry with Hofmeister and Hospital work with Naunyn, all at Strassburg (1900-1902) and later spent a year at the University of Berlin under Emil Fischer and in plant physiology under Kny. One vacation was spent at Frankfort a/M with Ehrlich, Edinger and Noorden, and another in clinical medicine with Kuttner, Piorkowski and others.

Since returning from Germany, Dr. Alsberg has served as Assistant in Physiological Chemistry in the Medical School of Harvard University (1902-1905); Secretary of the Section of Physiological Chemistry of the International Congress of Arts and Sciences, St. Louis Exposition; Instructor and Head of Department of Biological Chemistry, Harvard Medical School (1905-1906); Faculty Instructor and Head of Department of Biological Chemistry, Harvard Medical School (1906-1908); Chemical Investigator of United States Bureau of Fisheries, investigating food values of sea foods (summers 1906-1908); Chemical Biologist in charge of Poisonous Plant Laboratory, Bureau of Plant Industry, U. S. Department of Agriculture (1908); Past Sec-



DR. CARL L. ALSBERG, NEW CHIEF OF BUREAU OF CHEMISTRY

retary and member of Council Boston Society of Medical Sciences; Chairman Section of Biological Chemistry of the American Chemical Society; Fellow of the American Association for the Advancement of Science. He is also a member of a number of scientific societies including The American Chemical Society, The American Physiological Society, the Society of Biological Chemists, the Society of Experimental Biology and Medicine, the Society of Pharmacology and Experimental Therapeutics, the American Pharmaceutical Association, the Washington Academy of Science; an associate member of the American Medical Association and the American Association of Cancer Research; and a member of the Corporation of the Marine Biological Laboratory at Wood's Hole, Massachusetts.

ELECTROLYTIC COPPER REFINING IN NORWAY

Consul General Charles Adams Holder, Christiania, states that for several months a company at Aamdal, Norway, has been successfully extracting copper from the crude ore by an electrolytic process invented by Victor Hybinethe, a Norwegian engineer, who has patented the process in Europe and the United States. The Aamdal works have proved so successful that plans are now under way for increasing the output to 3 tons of metallic copper per day.

The treatment, which is done at the mine and thus results in enormous shipping economies, consists in leaching the crushed ore with a solution of sulfuric acid which dissolves out the copper; a strong current of electricity is then passed through this solution and the pure copper is precipitated.

Experiments with copper pyrites from the Orkla and Sulitjelma mines, in which much foreign capital is invested, have been equally successful, and as a result will probably be treated by the Hybinethe process in the future. The ores were formerly shipped to Germany and Sweden, respectively, owing to their refractory character and to the lack of proper Norwegian reduction works, but of late the Sulitjelma company has not been able to mine with any profit by this plan, owing to the low price of copper and the costs of transportation. The new process will, therefore, mean a great deal to the copper industry of Norway.

GROWING USE OF AMMONIUM SULPHATE IN CHINA

Vice-Consul Charles F. Brissel, Amoy, reports that for many years Manchurian bean cake has been extensively employed as a fertilizer in the vicinity of Amoy, but since 1903 the use of sulfate of ammonia has become more common. To use the bean cake the farmer must pound the large cakes to a dust which must be soaked in water for three days before it can be used. The sulfate of ammonia dissolves in water almost immediately and thus can be used with greater facility. Of the two kinds of sulfate of ammonia, the pure white and the gray-reddish mixture having a strong odor, the latter is the kind used. Sulfate of ammonia is used in the Amoy district principally for fertilizing rice and sugar-cane fields. It is said to have four times the strength of the bean cake and to cost but three times as much, which, taken together with the added facility of application, creates a growing market. In 1903 a trial shipment of 53 pounds was received at Amoy. The imports for 1911 were 7,000 long tons, and up to October 31st the imports for 1912 amounted to about 9,000 long tons. The duty is 5 per cent. Sulfate of ammonia is imported in bags weighing about 175 pounds.

Vice-Consul Raymond S. Curtice, Dalny, Manchuria, states that the enormous output of the Fushun collieries is causing the owner, the South Manchuria Railway, no little anxiety, as the actual and probable demands do not justify the expectation that they will equal the output. Accordingly the manufacture of by-products has become a necessity. It is now proposed to begin the manufacture of sulfate of ammonia and producer gas. It is claimed that 100 tons of Fushun coal can produce 5 tons of sulfate of ammonia in addition to a large amount of gas. It is intended to put the sulfate of ammonia on the Japanese market in competition with the foreign variety, which totals about \$5,000,000 a year. The competition will, of course, practically drive the foreign products out of the market, as the Fushun collieries will have an unlimited supply of both material and fuel. The gas will be used for the generation of electric power.

AMERICAN CHEMICAL SOCIETY SPRING MEETING.

The Spring meeting of the American Chemical Society will be

held in Milwaukee, March 25th to 27th, inclusive. The Council will meet on the evening of March 25th. The titles of all papers intended for the meeting should be in the hands of Secretary Charles L. Parsons, Box 505, Washington, D. C., by March 7th, or in the hands of the secretaries of the various divisions by March 5th; otherwise they cannot find place on the program.

"THE PROGRESSIVE AGE" BECOMES "THE GAS AGE"

We note with pleasure the change indicated in the above title. The publishers are to be congratulated on this improvement since it is a step towards standardization of scientific current literature, both in size and name. The general appearance, composition, paper and printing of *The Gas Age* are noticeably in advance of its predecessor.

OBITUARY—ALFRED BELLAMY AUBERT

Professor Alfred Bellamy Aubert, one of the oldest members of the American Chemical Society, for thirty-five years professor of Organic Chemistry and head of the Department of Chemistry, University of Maine, died at his home, 118 East 62nd Street, New York City, November 12, 1912. He was born in New York of Alsatian parentage, in 1853. He received his chief undergraduate training at the Imperial Lyceum of Strasburg; specialized in Chemistry, under Crafts, at Cornell University, receiving the B.S. degree (1873) therefrom, and the M.S. degree (1874) from the University of Maine; engaged in chemical research, 1899-1900, Massachusetts Institute of Technology. Dr. Aubert was a frequent contributor to the *Journal of the American Chemical Society*; *Chemical News*; *American Monthly Microscopical Journal*; *Photographic Times*; *Chemical Engineer*; *Le Diatomiste*; *La revue generale de Chemie*; and co-editor with Dr. Allen Rogers of a work on Industrial Chemistry. Under special ruling he became a recipient of a Carnegie pension for teachers.

Intellectually and professionally, Dr. Aubert was strongly equipped, of keen insight, an artistic, accurate, rapid and resourceful laboratory worker and investigator. Broadly cultured, philosophic, a linguist, master of a clear, crisp yet polished English, he was nevertheless unambitious and careless of his great gifts. For this reason, and from ill health, only his associates knew his real worth; also for these reasons his contributions to English and French journals in his special fields of Chemistry and Microscopy were, though occasional, all too few. Probably of most of his work he made no notes. Of some there were outlines, left unfinished, as was his latest projected book—"The Microscope in Chemical Analysis and Research." His "Industrial Chemistry," of which he was the originator, associate editor and partial author, long projected, delayed, and personally unrevised because of failing strength, was issued but shortly before his death. It was probably the first definitely planned, though not first issued, of the recently appearing treatises in this chemical field, to embody the symposium-of-experts method.

In personality, Professor Aubert was as artless and open as a child, and evidenced a great and sympathetic heart, obvious to all who met him. For his intimate friends he had a passionate attachment which gripped them in unseverable bonds. Over his pupils his gentle sway was complete and time-enduring. For them his wide culture, accurate knowledge and enlivening scientific imagination were rich resources of profit and delight. To have met him was a privilege; to have known him was a life's enrichment; to have sat at his feet was an abiding inspiration. "We shall not look upon his like again."

W. F. JACKMAN

BOOK REVIEWS

A Handbook of Sugar Analysis. A practical and descriptive treatise for use in Research, Technical and Control Laboratories. By C. A. BROWNE, Ph.D., chemist in charge of the New York Sugar Trade Laboratory (formerly Chief of the Sugar Laboratory, U. S. Bureau of Chemistry, Washington, D. C., and Research Chemist of the Louisiana Sugar Experiment Station, New Orleans, La.). John Wiley & Sons, New York and London. 8vo. 977 pages, 200 figures. Cloth, \$6.00 net.

This unusually thorough and able treatise upon sugar analysis has been prepared by the author in recognition of the great expansion of knowledge of the subject within the past quarter century with the devising of instruments of greater accuracy, the improving of old methods and the discovery of new ones.

The range of sugar analysis is so broad that in the selection of methods the author has been guided by his own experience—a very extended one—in various research, technical and control laboratories.

In order to correct the tendency of inexperienced workers to make general use of methods having only limited applicability, the author has included with the description of each method a brief account of its applicability and limitations.

A rather novel feature is the account in Part II of the sugars themselves, their occurrence, properties and methods of synthesis, which is often of use in determining their individuality. The practical nature of the book is indicated in the first chapter, which immediately takes up the sampling of sugar and sugar products, discussing the best methods as well as the influences which affect the samples.

The various methods of determining moisture are next taken up and very fully discussed, with thorough accounts of the apparatus employed and the derivation of formulas for specific gravity, temperature, etc.

An interesting chapter on the refractometer and its use in sugar analysis follows, which presents this recently developed method with thoroughness.

The next two hundred or more pages deal with polarized light, polarimeters, saccharimeters, polariscope accessories, specific rotation of sugars, methods of simple and of invert or double polarization as well as special methods of saccharimetry. The wealth of material gathered here is great and its ready applicability very satisfactory. In the miscellaneous physical methods as applied to the examination of sugars are interesting discussions of viscosity, specific heat of combustion, osmotic pressure constants and displacement of freezing and boiling points. All these are treated mathematically as are all the other topics requiring such elucidation, and this will be found one of the most appreciated features of the work, placing the discussions on the highest plane of scientific treatment. The author says that probably no other class of organic compounds gives such a variety of reactions or forms so large a number of chemical derivatives as the sugars, and he proceeds to describe the many reactions of use in identifying the sugars, generically and individually. Eighty pages are next devoted to the reduction methods for determining sugars, with great detail as to reagents and manipulation, variations due to many causes and collateral matter of importance in the analytical methods described. Another chapter describes methods for the quantitative determination of pentoses, etc., the fermentation methods of determining sugars, the various colorimetric methods and methods of determining sugars by weighing as hydrazones and osazones. Combined methods and the analysis of sugar mixtures are treated with formulae, tables, examples and explana-

tions. This is one of the most exacting fields in sugar analysis and will be found very well set forth.

Under miscellaneous applications are considered the routine analyses of sugar factory products not previously dealt with, as ash, quotient of purity, extraction of juice from cane and beet, acidity and alkalinity, as well as methods for determining crystal contents giving preference to that of Koydl. Starch, dextrine and malt extracts analyses are briefly considered as well as maple sugar and syrup, fruits products and honey. The author usually indicates the most reliable of the methods given, with reasons for its preference.

The second part of the work, two hundred and sixty pages in extent, is devoted to a discussion of the occurrence, methods of preparation, properties and principal reactions of the thirty or more sugars which have been isolated from plant and animal substances and of their many allied derivatives. Beginning with the classification of the sugars and their formation in nature, the author explains the optical activities of the asymmetric carbon compounds. The various monosaccharides are next described with especial attention to Arabin, xylose, fucose and rhodose before taking up very fully, as their importance deserves, the hexoses including the glucoses, mannoses, starch, pectins, galactoses, etc.

Under the disaccharides, of course, sucrose occupies the place of prime importance and its physical, chemical and biological properties are carefully discussed in considerable detail. The action of enzymes on sucrose constitutes not the least interesting feature of this chapter. Maltose, representing like sucrose, important manufacturing interests, receives detailed consideration and lactose is not far behind in this respect.

The trisaccharides and tetrasaccharides are principally represented by raffinose, and stachyose, the former of which comes in for extended attention.

The amino sugars, of considerable theoretical interest, because of their forming one of the connecting links between the carbohydrates and the proteids, are described, as well as the cycloses, which are widely distributed in nature and form a connecting link between the sugars and the aromatic benzole ring derivatives. Inosites and quebrachite are interesting members of this group.

In the closing chapter of this encyclopedic book the author briefly describes the alcohols and the monobasic and dibasic acids which are derived from the sugars by reduction and by oxidation and which are constantly found associated with them in nature.

Following the text are twenty-five tables, occupying a hundred pages, such as are most generally useful in sugar laboratories. These tables are also published separately for the convenience of those who wish to make frequent use of them in practical work.

One of the interesting features of this book is the considerable amount of the author's original work evinced throughout the volume. His study of moisture absorption and loss by different grades of commercial sugars, his method of vacuum drying and the details of his carefully elaborated arrangements for constant temperature work are all of very practical value. His methods for determining dextrin and commercial glucose in honey and his formulae for analyzing sugar mixtures are admirable evidences of the author's able handling of these intricate questions.

Indeed the entire work is greatly to be commended for its depth and thoroughness, and although it occupies nearly a thousand pages it is concise and to the point throughout. The book is a mine of useful information to all those in any way

interested in the sugars or any of the allied substances. It is a classic of its kind that will always occupy a preëminent place in sugar literature. The hundreds of excellent illustrations add greatly to the text and are quite in keeping with the high character of the volume in all other respects. W. D. HORNE

Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines. By R. M. STRONG AND LAUSON STONE. Bulletin 43, Department of the Interior, Bureau of Mines. 236 pp. July, 1912.

Under the terms of the act establishing the Bureau of Mines, the Bureau interprets its vocation to include the investigation of the liquid fuel resources of the country both with respect to geological conditions and to economic use, and accordingly a series of tests were conducted in great detail on the use of gasoline in small engines, 10 to 15 H. P., and the results are compared with their performance on alcohol as a possible competitor of gasoline. It is the results of these tests that are reported in this bulletin, which contains detailed information and conclusions drawn therefrom, so presented as to constitute a valuable addition to the literature on the subject. The cost of these investigations, undoubtedly very high, would be an interesting consideration especially as there is serious doubt as to whether any commensurate benefit will follow, for without questioning the scientific value of the data, it is believed that it will have practically no influence on either the construction or use of these engines or on the economical relations of gasoline to alcohol as sources of fuel supply. Some of the more important conclusions are abstracted below but these give but an inadequate idea of the report, which should find a place in the library of every engineer and chemist.

The low heating value of completely denatured alcohol averages 10,500 B. T. U. per lb. or 71,900 B. T. U. per gallon, while the corresponding values for gasoline of specific gravity 0.71 to 0.73 are 19,200 B. T. U. per lb. and 115,800 B. T. U. per gallon. Comparing them, the low heating value of one lb. of alcohol is approximately 0.6 of that for gasoline. One lb. of gasoline requires approximately twice as much air for complete combustion as is required by alcohol, so the heating value of 1 cu. ft. of explosive mixture of alcohol-vapor and air, in combining proportions, is approximately equal for gasoline air as for alcohol air at about 80 B. T. U. per cu. ft., standard. The compression that such mixtures will stand without self-ignition in the cylinders of the small four-cycle engines are 70 lbs. per sq. in. above atmosphere of gasoline, and 180 lbs. for alcohol, and in all cases the maximum fuel economy corresponds to the use of these maximum available compressions.

The gasoline engine operating on the maximum available compression of 70 lbs. per sq. in. will when operated at the same compressions of alcohol give an increase of 10 per cent. of the power over that obtained from gasoline, but when the compression is changed to the 180 lbs. per sq. in. which the alcohol will stand, the engine will, on that fuel, give 30 per cent. more horsepower than when operated on 70 lbs. per sq. in., the limiting value for gasoline and on gasoline. With alcohol fuel and the maximum compression pressure of 180 lbs. per sq. in. maximum explosion pressures reach between 600 and 700 lbs. per sq. in., which is greater than small gasoline engines are ordinarily built to withstand, indicating that for the most economical use of alcohol higher compressions are needed and heavier construction will be required than is provided in existing gasoline engines.

The consumption of fuel per hour per H. P. for these small engines operating at the compressions ordinarily used for gasoline are in the ratio of 3 to 2 for alcohol as compared with gasoline, but when each fuel is used at its maximum allowable compression, the volumetric consumption of fuel per hour per H. P. is about the same for alcohol and gasoline and averages about

one pint at the rated load which is ordinarily 75 per cent. to 80 per cent. of the maximum. To secure the best consumption of either fuel at any load requires a hand adjustment of mixture, and time of ignition for each change, and without hand adjustment, engines operated by throttle governors can double their fuel consumption on $\frac{1}{3}$ load. The best fuel consumption found on engines of 10 to 15 H. P. are for gasoline 26 per cent and 28 per cent. on compressions of 70 and 90 lbs. per sq. in. respectively. For alcohol, efficiencies are 28 per cent., 39 per cent., 40 per cent. for compressions of 70, 180 and 200 lbs. per sq. in., indicating a slightly superior efficiency for alcohol over gasoline at the same compression, 28 as compared with 26 per cent. at 70 lbs.

The addition of water to explosive mixtures of gasoline vapor and air does not change the specific consumption for gasoline per hour per H. P. but does decrease the H. P. up to an amount of water equal to that of gasoline by weight. The allowable compression pressure is at the same time raised to about 140 lbs. from 70 lbs. without preignition. Introduction of water with denatured alcohol in quantities up to 50 per cent. increases specific fuel consumption a small amount and decreases the horsepower.

The report contains detailed information on the chemical and physical properties of gasoline and denatured alcohol as fuel and the apparatus and methods used in the test with the details of procedure and the conduct of test and conclusions of a technical character on the variables that control economy, efficiency, time of ignition and character of spark, jacket water temperature, engine speed, load variation, water addition to fuel and decrease of compression on the performance of the machine.

It is proposed in the future to carry out similar tests on the use of heavy fuel oils in internal combustion engines and on the performance of the oil gas producer. The probable cost of proposed tests might be presented to representatives of the industries concerned, for discussion as to the justification for the expenditure compared with the beneficial effects that may be expected to follow.

C. E. LUCKE

Textbook of Chemical Technology and Metallurgy, prepared by the coöperation of distinguished specialists, edited by Dr. Bernhard Neumann, published by S. Hirzel, Leipzig. (German.) 8vo. Price, \$5.00.

Since the title clearly indicated the character of this work, a textbook of Chemical Technology, we should not expect more than a general survey of the field of industrial chemistry and metallurgy. The authors cannot give more than the salient points in connection with each industry, including a few statistics to give an idea of the magnitude and of the growth of that particular line of chemical manufacture.

Accepting this work of Neumann and his collaborators in the above light, we have a book that comes up to the specifications in every respect, and in many chapters the development of the subject gives us more than we have a right to expect in a work of this character and scope.

Some idea of the space devoted to each of the various industries can be obtained from the following, selected at random as showing some of the smaller as well as some of the larger lines of chemical manufacturing: Sulphuric acid 25 pages, coke 10, acetylene 11, soda 29, chlorine 25, iron and steel 39, petroleum 11, rubber 18, glue 4, sugar 32.

The topics discussed, include: Water supply and disposal of waste effluents from factories, liquid air, oxygen, ozone and acetylene, fuels and illuminants, 114 pages; Salt, potash, soda, mineral acids, chlorine by Weldon and electrolytic methods, ammonia and cyanide compounds, 158 pages; Aluminium and compounds, magnesium, calcium, and barium compounds, peroxides and per salts, fertilizer chemicals, mortar, stoneware and porcelain, glass, 131 pages; Iron, steel and nonferrous metals,

139 pages; Explosives, petroleum, asphalt, coal tar and wood products, 67 pages; Fats, glycerine, and soaps, 34 pages; Rubber, glue, and leather, 34 pages; Sugar, starch, dextrine and the fermentation industries, 105 pages; Cellulose and artificial silk 14 pages, and finally, the textile fibers and dyestuffs, 48 pages.

A criticism that is too often applicable to books of this class, that the practice is out of date, cannot be made of the volume before us. One looks carefully for any omissions in connection with the latest developments of chemical industry and finds that the authors have informed themselves of the latest methods in all countries. A possible exception to the foregoing statement might be made with reference to petroleum distillation as modified by American conditions.

In this admirable work, one can find very little to criticize, if the intent of the authors is kept in mind, that of writing a textbook of general information on industrial chemistry and metallurgy. It might be said that the space devoted to the Talbot process of steel manufacture (six lines) is too short. In like manner, we should like to have seen more than a page devoted to alloy steels and their applications, the development of which has certainly produced a marvelous group of new materials for the modern industrial world.

The more important chapters conclude with statistics, which are in most cases brought down to the close of 1910, and which also show the production by countries.

The work comprises 890 pages, with 398 cuts and five plates. All of the figures are up-to-date, and in this connection it is certainly a relief to find that the old cuts, so long familiar because they were copied by generation after generation of textbook writers, have been replaced.

J. H. JAMES

Die Synthese des Kautschuks. RUDOLF DITMAR, Inhaber des Kautschuk-Laboratoriums und der Kautschuk-Chemischule in Graz. 124 + vii pages. Dresden and Leipzig: Verlag von Theodor Steinkopff, 1912.

This little book sketches briefly the work that has been done on synthetic rubber up to 1912. The matter is divided as follows: I. The Constitution of Rubber (23 pp). II. Synthesis of Rubber (9 pp). III. Preparation of Materials used in making Synthetic Rubber (22 pp). IV. The most important patents granted and applied for (70 pp). As the author foreshadows in his preface, the activity in this field of industrial research is such that by the time a résumé of this sort appears in print further progress will inevitably have been made. The monograph has been prepared primarily for the sake of those chemists not themselves actively engaged in this field. The work has been well done and will be read with interest.

THEODORE WHITTELEY

Soil Fertility and Fertilizers. By JAMES EDWARD HALLIGAN. 398 pp., 23 illustrations. The Chemical Publishing Co., 1912. Price, \$3.50.

The preface states that "this book has been written to be in reach of the student, manufacturer, and other persons interested in the subject of fertilizers. Technical terms have been omitted as much as possible."

The book is divided into sixteen chapters; the first treats of the chemical elements needed by plants, and the composition of plants including analyses of the principal agricultural crops.

Chapters II and III deal with the fertility of the soil and means of maintaining fertility.

Chapter IV takes up the question of farm manures and includes much valuable information concerning the composition of the various kinds, value, manner of application, etc.

The remaining twelve chapters discuss the fertilizer question in all of its phases including a very complete description of

the different fertilizer materials, where obtained, method of preparation, etc., together with a large amount of information relative to their functions as bearing on the production of crops.

The subject is a large one considered in all of its bearings, but the author has succeeded in bringing together just such facts as will enable one to get a very clear understanding of the usually accepted views concerning soil fertility and the compositions and functions of fertilizers. The volume is replete with tabulations and statistics which include valuable data concerning the analysis of fertilizers, farm crops, formulae, valuation, etc., which makes it valuable as a general reference book. The data is compiled from reliable sources, and excellent judgment has been used in selecting just such information as will appeal to those interested in the subject. The whole work is a useful one as a general treatise on the subject.

F. B. CARPENTER

Das Hydrosulfit. By DR. CARL JELLINEK. 2 parts, 8vo., pp. vi + 188 and viii + 230. Stuttgart, 1911. Ferdinand Enke. Price, Part I, 1.20 M.; Part II, 1.50 M.

These two monographs form portions of what might be termed a treatise on chemistry, a volume of which is issued each year by Prof. W. Herz, of Breslau.

The first part of the present treatise deals with the pure chemistry of hydrosulphurous acid and its various salts and compounds. The physical chemistry of the subject is also elaborated at considerable length, and with a thoroughness distinctly German in its academic treatment. The second part deals with the preparation and technical chemistry of the various hydrosulphite compounds, and the methods for their analysis.

Whereas the purely chemical side of this subject is treated by the author in an excellent manner, the technical part is dismissed somewhat negligently, showing that the author in this part did not have a good grasp of his subject. In fact the technical matter consists principally of a collection of patents, with all the indefinite verbosity of legal style. As the hydrosulphites are principally interesting by reason of their technical applications, it is to be regretted that the author did not better develop this side of the subject. As a study in pure chemistry, however, the book is exceedingly interesting.

A very good bibliography of the subject is also furnished, as well as a complete list of patent titles relating to the manufacture and use of hydrosulphites.

J. M. MATTHEWS

The Analysis of Paint and Varnish Products. By CLIFFORD DYER HOLLEY, M.S., Ph.D. First Edition. Small 8vo. viii + 292 pp. John Wiley & Sons, New York. 1912. Price, \$2.50.

In the earlier work, "The Analysis of Mixed Paints, Color Pigments and Varnishes" by Holley and Ladd published in 1908, is to be found a large part, probably the major part of the subject matter of the present volume. In some cases the matter is quite identical. There is, however, a considerable proportion of new matter and as a whole it furnishes a valuable work of reference to one engaged in the analysis of paints and varnishes. It is to be regretted that so little space is given to China Wood Oil which is at present one of the most interesting materials entering into the composition of paints and varnishes. Probably each manufacturer of paint or of varnish will find about this volume a different point to criticize as not in accord with his own ideas of the proper methods of testing such products, but the work sets forth with a fair degree of completeness the present state of this art as most analysts come in contact with it. The references to original articles are, however, not nearly as frequent or as complete as the reviewer thinks they should be.

PARKER C. McILHINEY

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

- Ceramic Chemistry.** By H. H. STEPHENSON. 8vo. Price, \$1.50. Davis Bros., London.
- Chemical Industry of the World, Directory of the.** 2nd edition. L. 8vo. 1200 pp. Price, \$5.00. Union Deutsche Verlagsgesellschaft, Berlin. (German.)
- Coal-tar and Ammonia, The Industry of.** By G. LUNGE AND H. KOEHLER. Vol. 2. 5th edition. 8vo. 1516 pp. Price, \$12.00. F. Vieweg & Sohn, Brunswick. (German.)
- Coke, The Manufacture of, and the By-products from the Distillation of Coal.** By A. SAY. 8vo. Price, \$3.50. Dunod & Pinat, Paris. (French.)
- Cyanide Practice.** By H. W. MACFARREN. 8vo., 291 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Electrochemical Industry of France.** (Translation.) By M. R. PITAVAL. 8vo. Price, \$2.25. Wilhelm Knapp, Halle. (German.)
- Electrochemistry, The Principles of.** By A. J. ALLMAN. 8vo. 527 pp. Price, \$4.50. Edward Arnold, London.
- Electroplating.** By WILLIAM R. BARCLAY AND CECIL H. HAINSWORTH. 8vo. 381 pp. Price, \$2.00. Edward Arnold, London.
- Elements, Detection, Determination and Separation of the Chemical. I.** By A. RUEDISUELE. 8vo. Price, \$6.00. Max Drechsel, Berne. (German.)
- Essential Oils: Scientific and Industrial Bulletin, Roure Bertrand, Filis; Oct., 1912.** Sm. 8vo. 191 pp. Roure Bertrands, Filis, Grasse.
- Food: American Pure Food and Drug Law.** By JAMES WESTERVELT. 8vo. 1535 pp. Vernon Law Book Co., Kansas City.
- Food Industry, The.** By K. VON BUCHKA. Vol. 2. 8vo. Price, \$15.00. Akademische Verlagsgesellschaft, Leipzig. (German.)
- Fuels, Liquid, their Production, Characteristics and Examination.** By L. SCHMITZ. 8vo. 168 pp. Price, \$1.50. Julius Springer, Berlin. (German.)
- History of Chemistry from the Earliest Times to the Present Day.** By JAMES CAMPBELL BROWN. 8vo. 543 pp. Price, \$2.75. J. & A. Churchill, London.
- Industry, Chemical, Bluecher's Manual for.** 8th edition, 1912-13. L. 8vo. 1450 pp. Price, \$3.75. Franz Siemenroth, Berlin. (German.)
- Leather Dyeing and Preparing.** (Translation.) By M. C. LAMB. 2nd edition. 8vo. Price, \$5.50. Julius Springer, Berlin. (German.)
- Mine Fires and How to Fight Them.** By JAMES W. PAUL. 8vo. 14 pp. U. S. Bureau of Mines, Miners' Circular 10.
- Paper Pulp, Dyeing of.** By J. ERFURT. 3rd edition. 8vo. Price, \$3.75. Carl Hofmann, Berlin. (German.)
- Petroleum and Kindred Substances; Vol. IV.** By H. VON HOFER. 3rd edition. Lex. 8vo. 351 pp. Price, \$3.75. F. Vieweg & Sohn, Brunswick. (German.)
- Practical Chemistry, Introduction to.** By F. B. AHRENS. 2nd edition. 8vo. Price, \$1.25. Ernst Heinrich Moritz, Stuttgart. (German.)
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- Sizing, The Materials Used in.** By W. F. A. ERMEN. 8vo. 119 pp. Price, \$1.25. Constable & Co., London.
- Smoke Abatement and City Smoke Ordinances.** By SAMUEL B. FLAGG. 8vo. 57 pp. U. S. Bureau of Mines, Bulletin 49.
- Technology, Chemical, and Metallurgy, Textbook of.** By BERNHARD NEUMANN. 8vo. Price, \$5.00. S. Hirzel, Leipzig. (German.)
- Textile Design and Color.** By WILLIAM WATSON. 8vo. Price, \$2.00. Longmans, Green & Co., New York.
- Water Purification and Sewage Disposal.** By J. TILLMANS. 8vo. Price, \$2.00. Wilhelm Knapp, Halle. (German.)
- Colors Used in the Cement Products and Artificial Stone Industries.** ANONYMOUS. *Farben Zeitung*, Vol. 18, 1912, No. 11, pp. 579-582.
- Concrete, Tests of Waterproofing for.** By CLOYD M. CHAPMAN. *Industrial World*, Vol. 46, 1912, No. 51, pp. 1504-1506.
- Cyaniding Slime Ore by Continuous Decantation.** By H. C. PARMELEE. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 1, pp. 25-28.
- Explosives, The Energy of.** By WALTER O. SNELLING. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 8, pp. 653-683 and *Engineering Record*, Vol. 67, 1913, No. 2, pp. 54-55.
- Fat, The Distillates of Wool.** By J. MARCUSSON AND A. VON SKOPNIK. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 50, pp. 2577-2580.
- Gas, Illuminating, in its Hygienic and Industrial Relations.** By AD SAMTLEBEN. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 51, pp. 2640-2649.
- Gas, Illuminating, Some Notes on the Purification of.** By R. H. BURDICK. *American Gas Light Journal*, Vol. 98, 1913, No. 1, pp. 1-7, 10-13.
- Lead Smelting, The Action of Lime in the Flintshire Process of.** By C. O. BANNISTER AND A. V. ATLEY. *Chemical World*, Vol. 2, 1913, No. 1, pp. 9-11.
- Lubricating Oil, Purchase of, by Specification.** By A. D. SMITH. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 8, pp. 684-722.
- Mercury, A Case of Mercurial Poisoning and the Estimation of, in Textile Materials.** By L. L. LLOYD AND W. M. GARDNER. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1109-1112.
- Mordants for Dyeing and Printing, Making of.** By T. BROCKLEHURST. *Textile Colorist*, Vol. 34, 1912, No. 408, pp. 311-314.
- Oils, Progress in the Domain of Ethereal, and Perfumery.** By A. RECLAIRE. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 50, pp. 2580-2589.
- Paint-Making Machinery.** By J. R. TORRANCE. *Oil and Colour Trades Journal*, Vol. 42, 1912, No. 735, pp. 1672-1677.
- Patent Law in 1911, Essays on.** By H. TH. BUCHERER, et al. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 49, pp. 2566-2576.
- Patent Protection for Pharmaceutical Products.** By JULIUS EPHRAIM. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 51, pp. 2629-2640.
- Peat for Power Purposes, Commercial Utilization of.** By H. V. PEGG. *Journal of the American Peat Society*, Vol. 5, 1912, No. 3, pp. 163-168.
- Photometry of Incandescent Gas Lamps, The.** By C. O. BOND. *American Gas Light Journal*, Vol. 97, 1912, No. 27, pp. 418-423, 426-427.
- Power-Plant Economics.** By HORACE W. FLASHMAN. *School of Mines Quarterly*, Vol. 34, 1912, No. 1, pp. 1-23.
- Rubber, India, Determination of Total Sulfur in.** By C. E. WATERS AND J. B. TUTTLE. *Bulletin of the Bureau of Standards*, Vol. 8, 1912, No. 3, pp. 445-453.
- Rubber, India, The Action of Gaseous Oxygen on.** By STANLEY JOHN PEACHEY. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1103-1105.
- Rubber, Natural and Synthetic.** By F. MOLLWO PERKIN. *India Rubber Journal*, Vol. 44, 1912, No. 25, pp. 15-17.
- Rubber, The Nitrogenous Constituent of Para Rubber, and its Bearing on the Nature of Synthetic.** By CLAYTON BEADLE AND HENRY P. HEVENS. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1099-1103.
- Sewage and Sewage Filter Effluents, Disinfection of.** By H. W. CLARK AND STEPHEN DE M. GAGE. *Engineering Record*, Vol. 67, 1913, No. 1, pp. 14-16.
- Sewage Pumping Machinery and Appliances.** By J. RALPH GIBSON. *Industrial World*, Vol. 46, 1912, No. 53, pp. 1568-1570.
- Sewage, The Purification of Tannery Effluents.** By F. P. VEITCH. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 1, pp. 10-22.
- Solvents, Physical Constants of some Chlorinated Hydrocarbons Important as.** By W. HERZ AND W. RATHMANN. *Chemiker Zeitung*, Vol. 36, 1912, No. 146, pp. 1417-1421.
- Sugar, Study of the Different Methods of Determining Sucrose in Cane Molasses.** By CHARLES FRIBOURY. *International Sugar Journal*, Vol. 14, 1912, No. 168, pp. 702-712.
- Sulfates, Anhydrous.** By G. CALCAGIN. *Gazzetta Chimica Italiana*, Vol. 42, Part 2, 1912, No. 6, pp. 652-686.
- Sulfur in Illuminating Gas, and its Removal with Special Reference to the Use of Lime.** By L. J. WILLIEN. *Gas Age*, Vol. 31, 1913, No. 1, pp. 5-14.

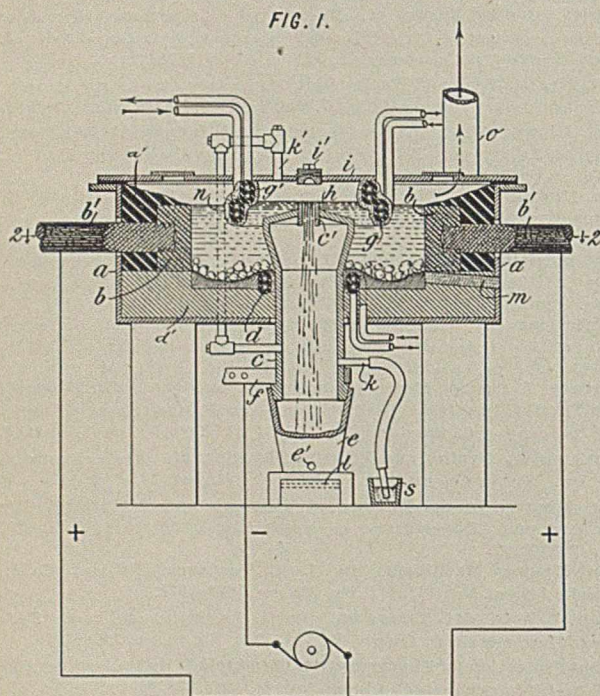
RECENT JOURNAL ARTICLES

- Alkaloid Chemistry in 1911.** By OTTO HUEBNER. *Chemiker Zeitung*, Vol. 36, 1912, No. 154, pp. 1493-1495.
- Alloys, Non-Ferrous, Test Bars for.** By JESSE L. JONES. *Transactions, American Institute of Metals*, Advance Copy, 1912, pp. 1-15.
- Analytical Chemistry, Present Status and Significance of.** By W. FRESENIUS. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 49, pp. 2513-2518.
- Bleaching of Cotton, Determination of the Degree of.** By C. PIEST. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 49, pp. 2518-2522.
- Boiler Scale, The "Luminator" Used for the Prevention of.** By E. E. BASCH. *Chemiker Zeitung*, Vol. 36, 1912, No. 148, pp. 1435.
- Cement, Portland, Constitution of.** By P. H. BATES. *Industrial World*, Vol. 46, 1912, No. 51, pp. 1544-1546.
- Coke, Manufacture, New Methods of.** By WILLIAM H. BLAUVELT. *Industrial World*, Vol. 46, 1912, No. 51, pp. 1516-1519.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Light Metals, Notably Sodium. Seward, von Kugelgen & von Bidder, Nov. 5, 1912. U. S. Pat. 1,043,154. The purpose of this process is to produce sodium directly by the electrolysis of sodium chlorid. In the apparatus shown, current is led through the casing *a* by means of graphite pencils, *b'*, which are connected with graphite plates, *b*, which fit together to form

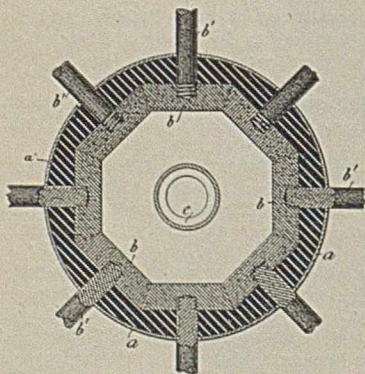


a polygonal anode and also form the sides of the crucible.

By limiting the height of the anode a protective layer of salt may be maintained over the top, preventing oxidation and disintegration of the carbon.

The cathode *c* is made of cast iron. Surrounding the cathode at a point above its entry through the casing is a water-cooled coil, *d*, which serves at once to prevent leakage of electrolyte and limits the activity of the cathode which otherwise would be progressively downward. This coil is embedded in the crucible bottom as shown and also tends to maintain the integrity of the latter by its cooling effect. A nipple, *c'*, in the top of the cathode receives the molten metal as its level rises within the sodium chamber and directs its course so that it will drop clear of the walls of the cathode cavity and fall into the receiver *e*, from whence it may be tapped at intervals through tap-hole *e'*.

FIG. 2.

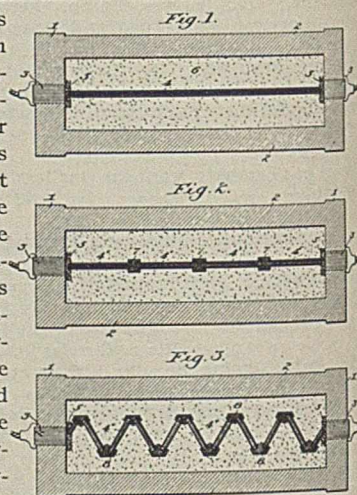


The sodium is collected within the water-cooled and salt-incrusted "curtain" *g*, which dips below the electrolyte and divides the space above it into a "sodium-chamber" and a "chlorin chamber." *g* is in no sense a "pole cell" as it is kept totally inactive by the layer of chilled salt, *n*, maintained thereon

through the cooling action of the water circulating within the "curtain." The "curtain" is made of two separate coils of copper tubing which are first covered with a solid insulating material before the layer of chilled salt is applied. Such a preliminary coating will act as an extra insulation in case the layer of salt becomes too thin through irregularities in the run and is conveniently made by closely wrapping two or more layers of strong asbestos twine on the tubes. An opening through the cover *i* at its center gives access to the sodium chamber and to the cathode cavity through the nipple *c'* and is normally closed by the plug *i'*. Other openings through the cover into the chlorin chamber are provided for feeding in salt and for breaking up salt crusts if any form. The chlorin is drawn out through the stack *o*, a slight suction being preferably maintained. The crucible may be quickly emptied when desired through the tap-hole *m*.

Silicon Carbide. F. J. Tone, Nov. 12, 1912. U. S. Pat. 1,044,295. In the commercial manufacture of silicon carbide a mixture of silica and carbon is subjected to heat in an electric furnace, the heating means being a resistance core of granular or pulverized carbon.

This core offers resistance not only by reason of the specific resistance of the carbon but also on account of the numerous points of poor contact between the discrete particles of carbon. The patentee has discovered that the efficiency of the process may be considerably increased by employing in place of the core of pulverized or granular carbon a continuous solid carbon consisting either of a single shaped piece or a series of pieces joined together in a manner to form the equivalent of a single piece.



Acetone and Higher Alcohol by Fermentation of Starch, Sugars and Other Carbohydrate Materials. A. Fernbach and E. H. Strange, Nov. 12, 1912. U. S. Pat. 1,044,368. In this process carbohydrate matter is mixed with water and a suitably degraded yeast added. The mixture is then sterilized, a ferment of the type of the butylic bacillus of Fitz added, and the mixture fermented in the absence of air.

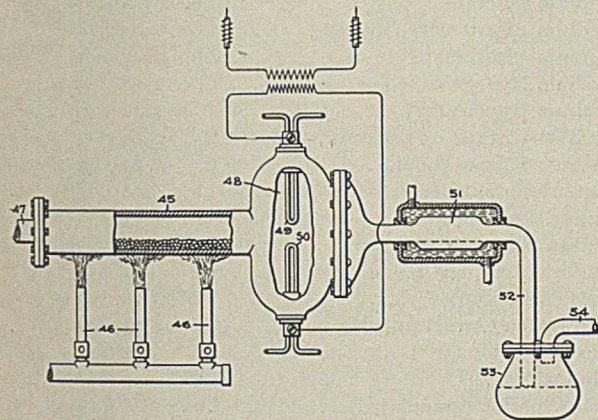
Reducing Chemical Compounds. Ezechiel Weintraub, Dec. 3, 1912. U. S. Pat. 1,046,043. In this process an electrical arc is utilized to effect chemical change, and to remove the reduction products from the zone in which this change is carried out.

Certain chemical compounds, as, for instance, chlorids and bromids, are to a certain extent reducible by hydrogen at high temperature, but the action is in many cases a reversible one; hence the yield of the reaction may be very small. According to this invention, the reverse reaction is prevented by the rapid removal of the reduction product from the active zone.

The process can be used in general for the reduction of chlorids and bromids which do not form solid sub-chlorids and sub-bromids, as, for instance, zirconium chlorid and boron chlorid,

and, in some cases, can also be used even when a sub-chlorid forms, as is the case with titanium chlorid.

In the use of the process applied for example, to boron chlorid, pure dry hydrogen is employed as a reducing agent and as a means for effecting the necessary temperature, and an electrical arc is maintained between suitable electrodes. The apparatus



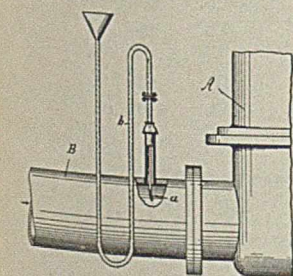
is so arranged that the arc blast drives the solid reduction product, namely, boron, out of the active zone and deposits it on the walls of the apparatus and on the electrodes. This is the only solid product present; the three other substances, boron chlorid, hydrogen and hydrochloric acid, being all gaseous, are allowed to pass on to an absorbing or condensing chamber.

The functions of the arc in removing the solid reduction product from the heated zone will be understood by appreciating that the emanations from the cathode spot move at high velocity and start the solid reduction productions at high velocity, without doubt very much higher than that of the slow moving gas.

Ethyl Alcohol from Sulfite Liquor. Gösta Ekström, Dec. 3, 1912. U. S. Pat. 1,046,160. The patentee's improvement consists in adding urine to the waste sulfite liquor to be fermented for the production of ethyl alcohol.

Treatment of the Residual Caustic Liquor Resulting from Digestion of Wood. J. M. Neil, Dec. 10, 1912. U. S. Pat. 1,047,132. In this process caustic liquor is recovered from the residual caustic liquor by treating it with an alkali metal compound of an acid-forming metal in the presence of carbonic acid to precipitate the organic matters present. The clear liquor is then separated, treated with ozone and causticized.

Regenerating Contact Masses. W. M. Kelsey, Dec. 17, 1912. U. S. Pat. 1,047,236. In catalytic or contact processes for the manufacture of sulfuric anhydrid, the platinized contact mass, in time, loses its original efficiency in a large measure and needs to be regenerated.

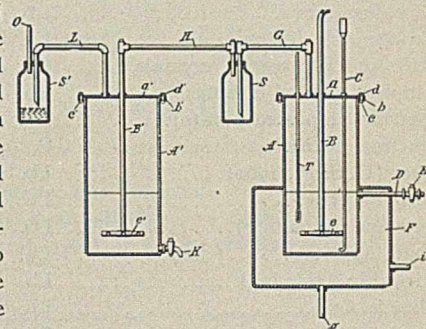


In carrying out this process there is passed through the contact mass to be regenerated, a volatilized mixture of nitric acid and hydrochloric acid, at such temperature that there will be no condensation while the volatilized mixture is passing through the mass. The mixture of nitric and hydrochloric acids is conveyed through the mass either by a current of air or a current of burner gas (*i. e.*, the mixture of SO₂ and air employed in the production of sulphuric anhydrid). The heat of the air or of the burner gas, as the case may be, is utilized to volatilize the mixture of nitric and hydrochloric acid employed. A temperature of 200° C. is feasible for the purpose, but for the best results it is desirable to pre-

heat either the air current or the burner gas current to from 450° C. to 500° C., or sometimes to even a higher temperature. In practice the mixture (*e. g.*, 20 quarts of water, 2 quarts of HNO₃, and 4 quarts of HCl) is caused to fill the funnel and trap *b*, whereupon the blower for furnishing the preheated air or burner gas to the pipe *B* is started; the whole mixture is added as fast as the small hole in the outlet of the tube *a* will permit.

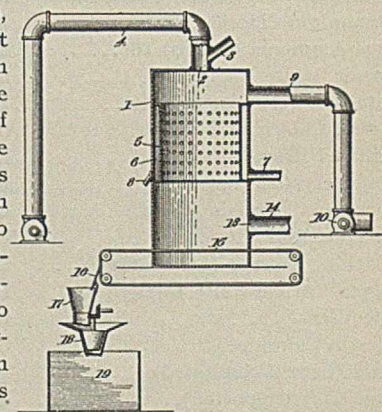
Solid Compound of Nitric and Sulfuric Anhydrids. W. Schultze. Dec. 17, 1912. U. S. Pat. 1,047,576. This composition is a solid crystalline compound containing sulfuric and nitric acids, or, more precisely, their anhydrids, chemically combined together. Mixtures of sulfuric and nitric acids are largely used for "nitrating," and have hitherto been supplied to the trade in liquid form, and more or less diluted state—*i. e.*, containing water sufficient to completely hydrate at least one of the two acid anhydrids contained in the mixture.

In producing this composition sulfur trioxid gas is added to a mixture of concentrated nitric acid and concentrated sulfuric acid until a solution is formed from which crystals can be deposited upon cooling, and the composition is allowed to cool.



Treatment of Starch. Neuberger and Bergh, Dec. 17, 1912. U. S. Pat. 1,047,831. In this process starch, in a powdered form and containing moisture preferably in the amount usually contained in green starch, is brought into contact with a body of live steam and dropped through the steam into a body of heated dry air below the steam. By this process the product is cooked in its own moisture so as to be wholly or partly gelatinized, and it is then immediately dried so as to reduce the gelatinized particles thrown down from the gelatinizing zone, thus fixing the particles in a hard, dry, gritty form. Following the drying of the particles, they are conveyed to a suitable disintegrator where they are broken to the desired degree of fineness and the starch is then ready for commercial use.

Purifying Coke. W. P. Simpson, Dec. 17, 1912. U. S. Pat. 1,047,845. In this process carbon monoxid is introduced into the retort for the purpose of eliminating sulfur and sulfurous compounds from the carbonaceous material under treatment.



Phosphoric Acid from Mineral Phosphates. F. S. Washburn, Dec. 17, 1912. U. S. Pat. 1,047,864. Mineral phosphates are ground, mixed with silica and carbon and heated to a fluid condition. The phosphorus gases driven off are mixed with air and the resulting phosphorus pentoxid dissolved in water.

Tanning Compound. J. H. McWhirter, Dec. 24, 1912. U. S. Pat. 1,047,968. Compositions containing alfalfa extract, gum gambier and sodium chlorid, singly or in mixtures.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JANUARY, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	20 ¹ / ₂	@	23
Acetic Acid (28 per cent.).....	C.	2.00	@	2.15
Acetone (drums).....	Lb.	16 ¹ / ₂	@	17 ¹ / ₂
Alcohol, grain (188 proof).....	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.).....	Gal.	50	@	52
Alcohol, denatured (180 proof).....	Gal.	40	@	42
Amyl Acetate.....	Gal.	2.65	@	2.85
Aniline Oil.....	Lb.	10 ¹ / ₈	@	10 ³ / ₈
Benzoic Acid.....	Lb.	23	@	27
Carbon Tetrachloride (drums).....	Lb.	9 ¹ / ₄	@	9 ³ / ₄
Carbon Bisulfide.....	Lb.	8 ¹ / ₂	@	9
Chloroform.....	Lb.	25	@	35
Carbolic Acid (drums).....	Lb.	14	@	15
Citric Acid (domestic), crystals.....	Lb.	38 ¹ / ₂	@	39
Camphor (refined in bulk).....	Lb.	44	@	—
Dextrine (imported potato).....	Lb.	6	@	7
Dextrine (corn).....	C.	2.75	@	3.06
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 ¹ / ₂	@	9 ¹ / ₂
Glycerine (dynamite).....	Lb.	18 ¹ / ₂	@	19
Oxalic Acid.....	Lb.	7 ¹ / ₈	@	8 ¹ / ₈
Pyrogallic Acid (bulk).....	Lb.	1.35	@	1.45
Salicylic Acid.....	Lb.	31	@	33
Starch (corn).....	C.	2.00	@	2.11
Starch (potato).....	Lb.	5 ¹ / ₄	@	5 ³ / ₄
Tannic Acid (commercial).....	Lb.	35	@	35 ¹ / ₂
Tartaric Acid crystals.....	Lb.	30 ¹ / ₄	@	31

INORGANIC CHEMICALS

Acetate of Lime (gray).....	C.	2.50	@	2.60
Acetate of Lead (brown, broken).....	Lb.	7 ³ / ₄	@	8
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate.....	C.	90	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 ¹ / ₂
Ammonium Chloride, gray.....	Lb.	6.15	@	6 ¹ / ₄
Aqua Ammonia (drums) 16°.....	Lb.	2 ¹ / ₄	@	2 ¹ / ₂
Arsenic, white.....	Lb.	4 ³ / ₄	@	5 ¹ / ₄
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Barium Chloride.....	C.	1.65	@	1.70
Barium Nitrate.....	Lb.	5	@	5 ¹ / ₄
Borax, crystals (bags).....	Lb.	3 ³ / ₄	@	4 ¹ / ₄
Boric Acid, crystals (powd.).....	Lb.	7	@	7 ¹ / ₂
Bromine, bulk.....	Lb.	25	@	30
Bleaching Powder (35 per cent.).....	C.	1.35	@	1.50
Barytes (prime white, foreign).....	Ton	18.50	@	22.50
Blue Vitriol.....	Lb.	5 ¹ / ₂	@	5 ³ / ₄
Calcium Chloride.....	C.	65	@	90
Chalk (light precipitated).....	Lb.	4	@	5
China Clay (imported).....	Ton	11.50	@	18.00
Feldspar.....	Ton	7.00	@	9.00
Fuller's Earth, powdered.....	C.	80	@	85
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.05	@	3.10
Lead Nitrate.....	Lb.	8 ¹ / ₈	@	8 ¹ / ₄
Lithium Carbonate.....	Lb.	65	@	70
Magnesite (raw).....	Ton	7.50	@	8.50
Nitric Acid, 36°.....	Lb.	3 ⁷ / ₈	@	4 ¹ / ₄
Phosphorus.....	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75.....	Lb.	21 ¹ / ₂	@	25 ¹ / ₂
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bromide.....	Lb.	35	@	37
Potassium Permanganate (bulk).....	Lb.	9 ¹ / ₂	@	10
Potassium Cyanide (bulk) 98-99%.....	Lb.	19	@	24
Potassium Iodide (bulk).....	Lb.	2.60	@	2.65
Potassium Chlorate, crystals.....	Lb.	10	@	10 ¹ / ₂
Potassium Nitrate (crude).....	Lb.	5	@	—
Potassium Bichromate, 50°.....	Lb.	6 ⁷ / ₈	@	7

Quicksilver, Flask.....	40.00	@	—	
Salt Cake (glass-makers').....	C.	55	@	65
Silver Nitrate.....	Oz.	40 ¹ / ₄	@	42
Soapstone in bags.....	Ton	10.00	@	12.00
Sodium Acetate.....	Lb.	4 ¹ / ₄	@	5
Sodium Chlorate.....	Lb.	8 ¹ / ₄	@	9 ¹ / ₄
Sodium Bicarbonate (English).....	Lb.	2 ³ / ₄	@	3
Sodium Bichromate.....	Lb.	5	@	5 ¹ / ₄
Sodium Hydroxide, 60 per cent.....	C.	1.60	@	1.65
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot.....	C.	2.60	@	—
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 ⁷ / ₈	@	7 ¹ / ₄
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	14 ¹ / ₄	@	14 ¹ / ₂
Tin Oxide.....	Lb.	52	@	54
Zinc Chloride (granulated).....	Lb.	4 ¹ / ₄	@	4 ¹ / ₂
Zinc Sulfate.....	Lb.	2 ¹ / ₄	@	2 ¹ / ₂

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 ¹ / ₂	@	14
Castor Oil (No. 3).....	Lb.	9 ¹ / ₂	@	10 ¹ / ₂
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5.80	@	5.85
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	37 ¹ / ₂	@	38
Cylinder Oil (light, filtered).....	Gal.	21 ¹ / ₂	@	32
Japan Wax.....	Lb.	9 ³ / ₄	@	10
Lard Oil (prime winter).....	Gal.	94	@	98
Linseed Oil (double-boiled).....	Gal.	44	@	—
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Paraffine (crude 120 & 122 m. p.).....	Lb.	3 ¹ / ₄	@	3 ¹ / ₄
Rosin Oil (first run).....	Gal.	34	@	36
Spindle Oil, No. 1.....	Gal.	18	@	19
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Stearic Acid (double-pressed).....	Lb.	9 ¹ / ₂	@	10 ¹ / ₄
Tallow (acidless).....	Gal.	65	@	68
Tar Oil (distilled).....	Gal.	30	@	31

METALS

Aluminum (No. 1 ingots).....	Lb.	25 ³ / ₄	@	26
Antimony (Hallet's).....	Lb.	9	@	10
Bismuth (New York).....	Lb.	2.10	@	2.15
Copper (electrolytic).....	Lb.	16.30	@	16.40
Copper (lake).....	Lb.	16 ¹ / ₂	@	—
Lead, N. Y.....	Lb.	4.20	@	4.30
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	46.00	@	—
Silver.....	Oz.	63	@	—
Tin.....	Lb.	50 ³ / ₄	@	—
Zinc.....	Lb.	7.20	@	7.30

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.30	@	—
Fish Scrap, domestic, dried.....	Unit	nominal		—
Blood, dried.....	Unit	2.75	@	—
Tankage, high grade.....	Unit	2.65	&	10
Bone, 4 ¹ / ₂ and 50, ground, raw.....	Ton	27.50	@	—
Potassium, "muriate," basis 80%.....	Ton	38.55	@	—
Phosphate, acid, 16 per cent.....	Ton	6.75	@	7.00
Phosphate rock, f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.75	@	4.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Pyrites, furnace size, imported.....	Unit	0.13 ¹ / ₄	@	0.13 ¹ / ₂
Castor meal.....	Unit	nominal		—
Mowrah meal.....	Ton	9.00	@	—